

## EVALUATION OF ADSORPTION OF URANIUM FROM AQUEOUS SOLUTION USING BIOCHAR MATERIALS

Wagner Clayton Corrêa\*<sup>1</sup>, Sabine Neusatz Guilhen<sup>1</sup>, Nilce Ortiz<sup>1</sup>, Denise Alves Fungaro<sup>1</sup>

<sup>1</sup>Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN - SP), Av. Professor Lineu Prestes 2242 - Cidade Universitária, 05508-000 - São Paulo/ SP

\*[wcorrea@ipen.br](mailto:wcorrea@ipen.br), [snguilhen@ipen.br](mailto:snguilhen@ipen.br), [notriz@ipen.br](mailto:notriz@ipen.br), [dfungaro@ipen.br](mailto:dfungaro@ipen.br)

### ABSTRACT

Uranium is present in the environment as a result of leaching from natural deposits and activities associated with nuclear fuel, copper mining, uranium mining, milling industry, etc. For the purpose of protecting ecosystem stability and public health, it is crucial to eliminate uranium from aqueous solutions before they are discharged into the environment. Various technologies have been used for removing U(VI) ions from aqueous systems. Among these methods, adsorption has been applied in wastewater because of simple operation procedure and high removal efficiency. Brazil is the largest producer of charcoal in the world, with nearly half of the woody biomass harvested for energy in Brazil being transformed into charcoal. Biochar exhibits a great potential as an adsorbent because of favorable physical/chemical surface characteristics. The objective of this work was to evaluate the adsorption potential of biochar materials prepared from pyrolysis of Bamboo (CBM), Eucalyptus (CEM) and Macauba (CMA) nuts for the removal of uranium from solutions. Adsorption experiments were carried out by a batch technique. Equilibrium adsorption experiments were performed by shaking a known amount of biochar material with 100 mL of U(VI) solution in Erlenmeyer flasks in a shaker at 120 rpm and room temperature (25 °C) for 24 h. The adsorbent was separated by centrifugation from the solution. The U(VI) concentration remaining in the supernatant solution was determined using inductively coupled plasma optical emission spectrometry (ICP-OES). The influences of different experimental parameters such as solution pH and bioadsorbent dose on adsorption were investigated. The highest uranium adsorption capacity were obtained at pH 3.0 and 16 g/L biomass dosage for CMA, pH 3.0 and 12 g/L biomass dosage for CBM and pH 2.0 and 10 g/L biomass dosage for CEM. The results demonstrated that the biomass derived char can be used as a low-cost adsorbent for removal of uranium from wastewater.

## 1. INTRODUCTION

Many activities produce radioactive aqueous wastes that require treatment before they get discharged into the environment [1, 2]. The removal and recovery of uranium from aqueous solutions is of paramount importance for the treatment of wastewaters arising as a consequence of many activities, but mainly those associated with the nuclear fuel cycle (mining, milling, conversion, enrichment and fuel fabrication).

Conventional treatment techniques such as chemical precipitation, reverse osmosis, solvent extraction, micellar ultrafiltration and adsorption are usually applied for the remediation of uranium from aqueous solutions [3, 4, 5, 6, 7, 8]. Due to its high efficiency and ease of handling, adsorption has been gradually applied for this purpose [9, 10].

Carbonaceous materials have been increasingly used as adsorbent, because of their higher thermal radiation resistance, compared with organic exchanger resins, and also their acid-base stability, compared with inorganic sorbents [10]. Produced by hydrothermal carbonization, biochar has been used as an alternative adsorbent for the removal of heavy metal ions from aqueous solutions [11], mostly because of its unique features, such as higher surface area and porous properties [12].

The aim of this study is to evaluate the removal of U(VI) from aqueous solutions using biochar materials produced by the pyrolysis of Bamboo, Eucalyptus and Macauba nuts.

## 2. MATERIALS AND METHODS

### 2.1. Materials

A standard solution of 928 mg/L of uranyl nitrate was prepared by dissolution of  $U_3O_8$  nuclear pure obtained from Center for Chemistry and Environment at the Nuclear and Energy Research Institute (CNEN/IPEN-SP), Brazil. Other U(VI) nitric solutions were prepared by diluting standard solution in double-distilled water. The biochar materials were prepared from pyrolysis of Bamboo (CBM), Eucalyptus (CEM) and Macauba (CMA) nuts.

### 2.2. Adsorption experiments

Adsorption experiments were carried out by a batch technique. Equilibrium adsorption experiments were performed by shaking a known amount of biochar material with 100 mL of U(VI) solution in Erlenmeyer flasks in a shaker at 120 rpm and room temperature (25 °C) for 24 h. The adsorbent was separated by centrifugation from the solution.

The U(VI) concentration remaining in the supernatant solution was determined using inductively coupled plasma optical emission spectrometry (ICP-OES). The adsorption of U(VI) was studied as a function of pH and bioadsorbent dose. The initial pH was adjusted with 0.1 mol L<sup>-1</sup> HNO<sub>3</sub> and 0.1 mol L<sup>-1</sup> NaOH.

The adsorption capacity ( $\text{mg g}^{-1}$ ) 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 ( $\text{mg L}^{-1}$ );  $V$  the volume of the adsorbate solution added (L) and  $M$  the amount of the adsorbent used (g).

Through the following equation (Eq. (2)), it was possible to determine the extraction efficiency in the different experiments performed:

$$R (\%) = \left( \frac{C_0 - C_t}{C_0} \right) \times 100 \quad (2)$$

where  $R$  is the efficiency of extraction or retention percentage,  $C_0$  ( $\text{mg L}^{-1}$ ) is the initial concentration of each adsorbate and  $C_t$  ( $\text{mg L}^{-1}$ ) represents the concentration of the adsorbate at time  $t$ .

### 2.3. Instrumental parameters

The quantification of uranium was carried out using a Spectro Arcos<sup>CCD</sup> inductively coupled plasma optical emission spectrometer (Spectro Analytical Instruments Co, Kleve, Germany) with an axially viewed plasma configuration and a radio frequency generator based on a free-running 27.12 MHz, enabling adjustments of power between 700 W to 1700 W. The spectrometer is equipped with simultaneous charge-coupled-device detectors (CCDs), which allow measurements from 130 to 770 nm. Table 1 summarizes the optimized measurement parameters.

**Table 1: ICP OES ARCOS Operating parameters**

Parameter	Value
Plasma gas flow	12 L min <sup>-1</sup>
Auxiliary gas flow	0.8 L min <sup>-1</sup>
Nebulizer gas flow	0.8 L min <sup>-1</sup>
RF power	1400 W
Plasma view	Axial
Peristaltic pump flow rate	30 Rpm
Spray chamber	Cyclonic
Nebulizer	Meinhard concentric nebulizer
Torch	Quartz
Replicates	3

The Background Equivalent Concentration for Mn and P was calculated using aqueous solutions of 0.1  $\text{mg L}^{-1}$  and 7  $\text{mg L}^{-1}$ , respectively. The emission line selected for uranium quantification was 409.014 nm.

### 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. It is well known that the species of uranium are strongly dependent on pH value [13]. The pH values were varied between 2.0 and 8.0, keeping the other parameters constant.

The influence of pH on the removal of uranium ions onto biochar materials was presented in Tables 2-4. The removal percentage was in the range of 17.2 to 32.9% for CBM, 0.80 to 19.6% for CMA and 88.7 to 81.0 for CEM, when pH was increased from 2 to 8, respectively.

**Table 2: The influence of pH on the removal of uranium ions onto CBM**

Initial pH	$q_t$ (mg g <sup>-1</sup> )	R (%)
2.04	0.100	17.2
3.08	0.187	32.1
3.93	0.053	9.09
5.03	0.139	23.8
5.91	0.070	13.0
7.04	0.105	19.0
7.93	0.186	32.9

**Table 3: The influence of pH on the removal of uranium ions onto CMA**

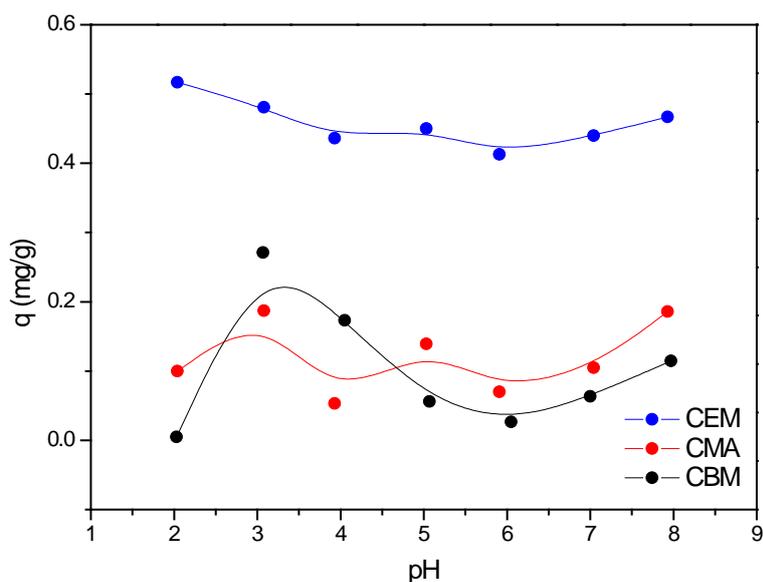
Initial pH	$q_t$ (mg g <sup>-1</sup> )	R (%)
2.03	0.0047	0.804
3.07	0.271	46.4
4.05	0.173	29.6
5.07	0.0561	9.60
6.05	0.0267	4.57
7.00	0.0636	10.9
7.97	0.115	19.6

**Table 4: The influence of pH on the removal of uranium ions onto CEM**

Initial pH	$q_t$ (mg g <sup>-1</sup> )	R (%)
2.04	0.517	88.7
3.08	0.481	82.5
3.93	0.436	74.8
5.03	0.450	77.2
5.91	0.413	71.9
7.04	0.440	76.5
7.93	0.467	81.1

Fig. 1 shows the comparison of uranium adsorption capacities for different biochar materials with variation of initial pH. As can be seen from Fig. 1, the adsorption ability of uranium by the biochar materials is significantly dependent on the pH value for CMA and CBM and almost constant for CEM.

The uptake amount of U(VI) reached the maximum adsorption capacity at pH 3.0 for both CMA and CBM and at pH 2.0 for CEM. The observed behaviour 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. At lower pH values ( $\text{pH} < 5$ ), the predominant species is  $\text{UO}_2^{2+}$ .



**Fig. 1. Effect of initial pH on the adsorption capacity of U(VI) onto biochar materials from Bamboo (CBM), Macauba (CMA) and Eucalyptus (CEM) ( $[U] = 5.8 \text{ mg/L}$ ; adsorbent dose:  $10 \text{ g/L}$ ; contact time:  $24 \text{ h}$ , temperature:  $25 \pm 2 \text{ }^\circ\text{C}$ )**

### 3.2 Effect of adsorbent dosage

The adsorbent dosage is an important parameter because it is associated to the determination of the capacity of an adsorbent for a given concentration of adsorbate. The adsorption studies of U(VI) onto biochar materials were done by varying the adsorbent dose from 10 g/L to 20 g/L. The equilibrium amount adsorbed and the removal efficiencies are presented in Tables 5-7.

**Table 5: The influence of dose on the removal of uranium ions onto CBM**

Dose (g/L)	$q_t$ (mg/g)	Removal (%)
10	0.082	14.1
12	0.053	11.0
14	0.214	51.2
16	0.236	64.6
18	0.084	25.9
20	0.044	15.1

**Table 6: The influence of dose on the removal of uranium ions onto CMA**

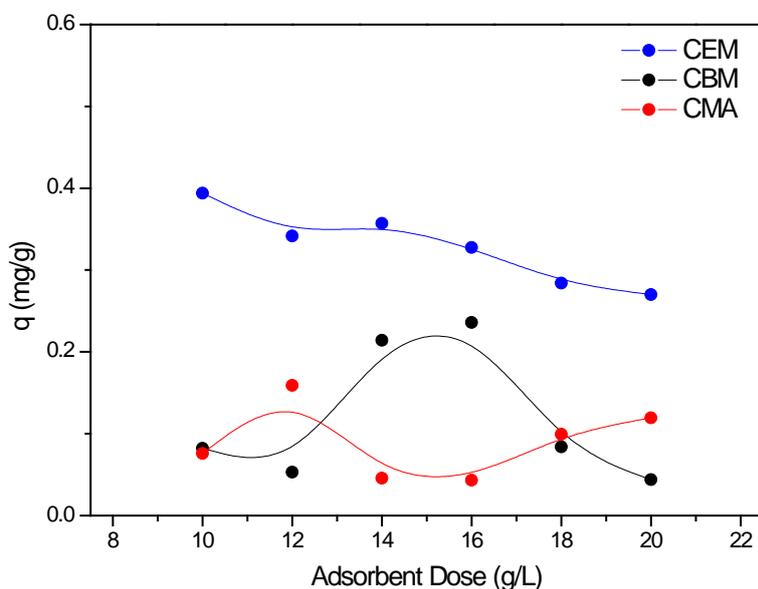
Dose (g/L)	$q_t$ (mg/g)	R (%)
10	0.0760	13.0
12	0.159	32.8
14	0.0456	11.0
16	0.0431	11.8
18	0.0994	30,7
20	0.120	41.0

**Table 7: The influence of dose on the removal of uranium ions onto CEM**

Dose (g/L)	$q_t$ (mg/g)	R (%)
10	0.394	67,2
12	0.342	70.0
14	0.357	85.3
16	0.328	89.4
18	0.284	87.2
20	0.270	92.2

The influence of adsorbent dosage on adsorption of U(VI) ion is shown in Fig. 2. Increasing the adsorbent dose up to 16 g/L and 12 g/L for CMB and CBA, respectively, increase the adsorption capacity (the amount adsorbed per unit mass of adsorbent) of metal ions, which is due to the increasing in adsorption sites of adsorbent material resulting from increasing of surface area of adsorbent [14]. However, further increase of adsorbent dosage does not afford exhaustive adsorption of U(VI). For CEM, when the dose was increased from 10 to 20 g/L, the adsorption capacity decreased.

The drop in adsorption capacity is mainly due to the sites remaining unsaturated during the adsorption process and can be mathematically explained [15]. Another reason may be attributed to the particle interactions, such as aggregation, caused by high adsorbent concentration [16]. Such aggregation would lead to a decrease in the total surface area of the adsorbent [17].



**Fig. 2. Effect of adsorbent dose on the adsorption of U(VI) onto biochar materials from Bamboo (CBM), Macauba (CMA) and Eucalyptus (CEM) ( $[U]= 5.8 \text{ mg/L}$ ;  $pH: 4.3$ ;  $\text{contact time: } 24 \text{ h}$ ,  $\text{temperature: } 25 \pm 2 \text{ }^\circ\text{C}$ )**

#### 4. CONCLUSION

The obtained results indicate that biochar materials prepared from pyrolysis of Bamboo, Eucalyptus and Macauba nuts can be used for the removal of uranium ions from liquid wastes. A batch technique was employed to investigate the adsorption behavior of U(VI) onto biochar materials from aqueous solutions as a function of initial pH of aqueous solution and adsorbent dose. The highest uranium removal efficiencies varied between 67% and 92% and were obtained with Eucalyptus adsorbent material.

## REFERENCES

- [1] K. SAKR, M. S. SAYED, M. B. HAFEZ, "Immobilization of radioactive waste in mixture of cement, clay and polymer," *J Radioanal Nucl Chem*, v. 256, n. 2, pp. 179–184, 2003.
- [2] T. OZDEMIR, A. USANMAZ, "Use of poly(methyl methacrylate) in radioactive waste management: I, radiation stability and degradation." *Prog Nucl Energy*, v. 51, n. 2, pp. 240–245, 2009.
- [3] Z. DJEDIDI, M. BOUDA, M. A. SOUISSI, R. BEM CHEIKH, G. MERCIER, R. D. TYAGI, J. F. J. BLAIS, "Metals removal from soil, fly ash and sewage sludge leachates by precipitation and dewatering properties of the generated sludge" *Hazard Mater*, v. 172, n. 2-3, pp. 1372–1382, 2009.
- [4] A. A. ABDEL-KHALEK, M. M. ALI, R. M. ASHOUR, A. F. J. ABDEL-MAGIED, "Chemical studies on uranium extraction from concentrated phosphoric acid by using PC88A and DBBP mixture," *J. Radioanal Nucl Chem*, v. 290, n. 2, pp. 353–359, 2011.
- [5] N. KUMARI, D. R. PRABHU, P. N. PATHAK, A. S. KANEKAR, V. K. J. MANCHANDA, "Extraction studies of uranium into a third-phase of thorium nitrate employing tributyl phosphate and dihexyl octanamide as extractants in different diluents", *J. Radioanal Nucl Chem*, v. 289, n. 3, pp. 835–843, 2011.
- [6] C. COJOCARU, G. ZAKRZEWSKA-TRZNADEL, A. JAWORSKA, "Removal of cobalt ions from aqueous solutions by polymer assisted ultrafiltration using experimental design approach, Part 1: Optimization of complexation conditions," *J Hazard Mater.*, v. 169, pp. 599–609, 2009.
- [7] C. COJOCARU, G. ZAKRZEWSKA-TRZNADEL, A. MISKIEVICZ, "Removal of cobalt ions from aqueous solutions by polymer assisted ultrafiltration using experimental design approach, Part 2: Optimization by hydrodynamic conditions for a cross-flow ultrafiltration module with rotating part," *J. Hazard Mater.*, v. 169, pp. 610–620, 2009.
- [8] T. P. RAO, P. METILDA, J. M. GLADIS, "Preconcentration techniques for uranium (VI) and thorium (IV) prior to analytical determination," *Talanta*, n. 68, pp. 1047–1064, 2006.
- [9] S. J. COLEMAN, P. R. CORONADO, R. S. MAXWELL, J. G. REYNOLDS, "Granulated activated carbon modified with hydrophobic silica aerogel-potential composite materials for the removal of uranium from aqueous solutions," *Environ Sci Technol*, v. 37, n. 10, pp. 2286–2290, 2003.
- [10] Y. S. ZHAO, C. X. LIU, Z. CHEN, S. Q. LI, G. TIAN, L. WANG, J. B. HUANG, S. J. LI, "Solid phase extraction of uranium (VI) onto benzoylthiourea-anchored activated carbon," *J Hazard Mater*, v. 176, n. 1-3, pp. 119–124, 2010.
- [11] M. KILIÇ, Ç. KIRBIYIK, Ö. ÇEPELIOGULLAR, A. E. PÜTÜN, "Adsorption of heavy metal ions from aqueous solutions by bio-char, a by-product of pyrolysis," *Applied Surface Science*, v. 283, pp. 856–862, 2013.

- [12] N. CAO, H. DARMSTADT, C. ROY, “Activated carbon produced from charcoal obtained by vacuum pyrolysis of softwood bark residues” *Energy & Fuels*, v. 15. Pp. 1263–1269, 2001.
- [13] T. MISSANA, M. GARCÍA-GUTIÉRREZ, V. FERNÁNDEZ, “Uranium (VI) sorption on colloidal magnetite under anoxic environment: experimental study and surface complexation modelling,” *Geochimica et Cosmochimica Acta*, v. 67, n. 14, pp. 2543–2550, 2003.
- [14] A. E. OFOMAJA, Y. S. HO, “Equilibrium sorption of anionic dye from aqueous solution by palm kernel fiber as sorbent,” *Dyes Pigm.*, v. 74, pp. 60–66, 2007.
- [15] B. ROYER, N. F. CARDOSO, E. C. LIMA, V. S. O. RUIZ, T. R. MACEDO, C. AIROLDI, “Organofunctionalized kenyaite for dye removal from aqueous solution,” *J. Colloid Interf. Sci.*, v. 336, p. 398-405, 2009.
- [16] M. ÖZACAR. I. A. SENGIL, “Adsorption of metal complex dyes from aqueous solutions by pine sawdust,” *Biores. Technol.*, v. 96, pp. 791-795, 2005
- [17] A. SHUKLA, Y. H. ZHANG, P. DUBEY, J. L. MARGRAVE, S. S. SHUKLA, “The role of sawdust in the removal of unwanted materials from water,” *J. Hazard. Mater.*, v. 95, pp. 137-152, 2002.