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Uranium removal from aqueous solution using macauba endocarp-derived biochar: Effect of physical activation

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1 **URANIUM REMOVAL FROM AQUEOUS SOLUTION USING MACAUBA**

2 **ENDOCARP-DERIVED BIOCHAR: EFFECT OF PHYSICAL ACTIVATION**

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ABSTRACT

The main aim of this study was to evaluate options for addressing two pressing challenges related to environmental quality and circular economy stemming from wastage or underutilization of abundant biomass residue resources and contamination of water by industrial effluents. In this study we focused on residues (endocarp) from Macaúba palm (*Acrocomia aculeata*) used for oil production, its conversion to activated biochar, and its potential use in uranium (U) removal from aqueous solutions. Batch adsorption experiments showed a much higher uranyl ions (U(VI)) removal efficiency of activated biochar compared to untreated biochar. As a result of activation, an increase in removal efficiency from 80.5 % (untreated biochar) to 99.2 % (after activation) was observed for a 5 mg L^{-1} initial U(VI) concentration solution adjusted to pH 3 using a 10 g L^{-1} adsorbent dosage. The BET surface area increased from 0.83 to 643 m^2 g^{-1} with activation. Surface topography of the activated biochar showed a very characteristic morphology with high porosity. Activation significantly affected chemical surface of the biochar. FTIR analysis indicated that U(VI) was removed by physisorption from the aqueous solution. The adsorbed U(VI) was detected by micro X-ray fluorescence technique. Adsorption isotherms were employed to represent the results of the U adsorption onto the activated biochar. An estimation of the best fit was performed by calculating different deviation equations, also called error functions. The Redlich-Peterson isotherm model was the most appropriate for fitting the experimental data, suggesting heterogeneity of adsorption sites with different affinities for uranium setting up as a hybrid adsorption. These results demonstrated that physical activation significantly increases the adsorption capacity of macauba endocarp-derived biochar for uranium in aqueous solutions, and therefore open up a potential new application for this type of waste-derived biochar.

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46

Main finding of the work:

This study has shown that a low-cost biomass, such as macauba palm endocarp, can be successfully converted to activated biochar by physical activation and efficiently used in the treatment of industrial effluents containing U(VI).

51

1. INTRODUCTION

Activated carbon can be defined as an amorphous solid of high porosity and high specific surface area. Well-known adsorbents of widespread use, activated carbons have many applications, including purification and remediation of polluted water, treatment of liquid and gaseous industrial effluents, gas storage and delivery (methane and hydrogen), metal recovery, catalysis, and biomedical applications, among others (Bandosz, 2006; Bansal and Goyal, 2005; De Celis et al., 2009; Kwiatkowski, 2011; Le Cloirec and Faur-Brasquet, 2008; Marsh and Reinoso, 2006; Mezohegyi et al., 2012; Nunell et al., 2012; Ramanujan et al., 2007; Rivera-Utrilla et al., 2011; Wang and Kaskel, 2012). Growing concerns surrounding environmental pollution have led to an increased demand for activated carbon in water treatment and sewage treatment applications. The global activated carbon market size was estimated at USD 4.72 billion in 2018 and it is expected to expand at a compound annual growth rate of 17.5% between 2019 and 2025 (Grand View Research, 2019; Roman et al., 2013).

The properties of activated carbon depend on the nature of the raw material used, the type of activation agent and the conditions of both the pyrolysis process and the activation itself. Characteristics such as shape, particle size, pore-volume, surface area, microporous structure, pore size distribution, physical and chemical characteristics of the surface define the properties and applicability of the activated carbon produced. It is possible to obtain different types of activated carbon with the modification of these parameters, making them more specific for a particular use (Rocha et al., 2006).

76   As a result of oxidation of surface functional groups, activated carbons typically have a

77   non-polar or weakly polar surface (Yang, 2013). This way, it is widely used to purify,

78   detoxify, deodorize, filter, discolor and remove a range of liquid and gaseous materials.

79

80   Almost all solid carbonaceous material can be converted to activated carbon. However,

81   some characteristics must be taken into account when choosing the raw material, such

82   as carbon content. The raw material must be high in carbon and low in inorganic matter

83   (ash). Other important factors are the cost and availability of the raw material. Recently,

84   agricultural residues have aroused a great deal of interest in the production of activated

85   biochar, because they originate from renewable and low-cost resources (Chen et al.,

86   2011; Kalderis et al., 2008). In this way, agricultural residues that would be normally

87   discarded gained a new potential for usability, being transformed into valuable products,

88   such as activated carbons.

89

90   The process of production of activated carbon typically involves three steps: the

91   preparation of the raw material, carbonization, and activation. In each of these steps, the

92   control of the operational conditions is decisive for the structural properties of the final

93   product.

94

95   Preparation of raw material consists of removing any dirt or foreign residue that does

96   not belong to the material. It also involves steps of grinding, for highest homogeneity

97   during thermal decomposition, and oven-drying in advance of carbonization.

98

99   Carbonization consists of thermal treatment (pyrolysis) of the precursor material (raw

100   material) in an inert atmosphere, at a temperature above 200 °C. In this step, the volatile

101   components and light gases (CO, H_2, CO_2 and CH_4) are removed, leaving behind a

102   porous carbon structure amenable to subsequent activation (Claudino, 2003). Biochars

103   obtained from lignocellulosic materials are essentially microporous. However, these

104   pores are often fully or partially filled by thermal decomposition products, such as tar

105   (Rodriguez-Reinoso and Silvestre-Albero, 2016). Activation promotes the removal of

106   organic compounds as well as other residues that can obstruct the pores of the biochar,

107   forming sites with enhanced adsorptive capacity (Rocha et al., 2006).

108

109   The activation process impacts on the basic characteristics of the material, such as pore

110   distribution and volume, density, specific surface area, and mechanical strength.

111   Activation exposes the aromatic groups to the oxidizing agents and initiates the

112   development of the microporous structure, characterizing the first phase of the process.

113   In the second phase, the decomposition of the walls among adjacent pores promotes

114   pore increase and the creation of large pores (Yang, 2013).

115

116   Activation can be carried out by chemical and physical processes. Chemical activation

117   relies on the action of inorganic additives, such as H_3PO_4, HNO_3, $ZnCl_2$, H_2SO_4, $NaOH$,

118   among others, to degrade and dehydrate the lignocellulosic material and,

119   simultaneously, inhibit contraction during carbonization (Mestre and Carvalho, 2018). It

120   consists of the impregnation of these activating agents into the not yet carbonized

121   material. The impregnated material is then carbonized (between 400-800 °C) in the

122   absence of oxygen (Contescu et al., 2018).

123

124   Activating agents generally have a dehydrating property, providing the formation of

125   crosslinks, rendering the material less prone to volatilization when heated to elevated

126   temperature. In this way, the formation of bituminous compounds inside the pores is

127   inhibited. The product is cooled and washed to remove the remainder of the activating

128   agent. In calcination, the chemical agents dehydrate the carbonaceous matter, resulting

129   in the creation of the pores. Peng et al. (2017) managed to enhance Cu(II) and Cd(II)

130   adsorption by modifying biochars with H_3PO_4. Trakal et al. (2014) used KOH activating

131   agent to enhance Cu(II) adsorption onto brewers draft biochar. Hadjittofi and Pashalidis

132   (2015) used HNO_3 oxidation in cactus fibers biochar for U(VI) adsorption from aqueous

133   solutions. Wu et al. (2019) used Fe(II, III) modified rice straw-derived biochar in soils

134   to retain phosphorous. The authors found that the adsorption capacity of Fe(II)-biochar

135   was 2.4 times higher than biochar without any Fe. Recently, Teng et al. (2020)

136   employed pinecone biochar as an adsorbing material. They found that this material has

137   great potential to adsorb Cd(II), reaching a maximum of 92.7 mg g^{-1} of capacity. The

138   review from Xiong et al. (2019) highlighted that biochar is considered an emerging low-

139   cost adsorbent, already been used to remove toxic elements such as Cr, Cu, As, and Pb

140   from water sources.

141

142   Physical activation, also called thermal activation, is the process of slow oxidation of

143   the char, through which it develops a porous structure, increasing its surface area. This

144   type of activation is performed after the carbonization process at a temperature between

145   700-1000 °C under appropriate flow of oxidizing gas (water steam or CO_2, used

146   individually or in combination). This process is also known as partial gasification

147   (Schettino Junior, 2004).

148

149   After physical or chemical activation, the activated biochar is subjected to subsequent

150   steps, such as cooling, sieving, washing, drying, polishing, granulometric separation and

151   packing.

152

153   Although chemical activation provides a greater yield, since it employs lower

154   temperatures and shorter activation time (Maciá-Agulló et al., 2004), the cost of

155   activating agents, combined with the additional washing step, may favor the use of

156   physical activation. The advantages of physical activation are the possibility of

157   developing a more porous structure with a larger active area, besides having a smaller

158   environmental impact in terms of secondary pollution generation. Rajapaksha et al.

159   (2015) reported the enhanced removal of sulfamethazine (SMT) from water by steam-

160   activated biochar synthesized from an invasive plant (*Sicyos angulatus* L.). Franciski et

161   al. (2018) used CO_2 activated biochar from solid wastes of a beer industry for

162   methylene blue adsorption. As reported by Zhang et al. (2019), sludge-based biochar

163   activated with CO_2 enhanced Pb(II) adsorption.

164

165   Activation is an essential tool for the production of biochar with higher specific surface

166   area and highly developed porosity, promoting the increase in the adsorption capacity

167   (Gorgulho et al., 2008). In the process of activation, it is desirable to obtain a product

168   with high internal surface area. In general, the product of activation presents a large

169   total pore volume and a high internal surface area in the range between 300 and 2500 m^2

170   g^{-1} (Yang, 2013).

171

172   Water molecules are much smaller than CO_2 molecules, which facilitates vapor

173   diffusion through the porous network. As a result, steam activation yields both

174   micropores and mesopores with a wider range of pore size distribution, whereas CO_2

175   activation essentially forms and widens micropores (Dalai and Azargohar, 2007; Feng

176   et al., 2018). Also, CO_2 activated biochar tends to be more thermally stable (Molina-

177   Sabio et al., 1996).

178

179   IEA-R1, the largest research nuclear reactor in Brazil, is located at the Nuclear and

180   Energy Research Institute (IPEN-CNEN/SP). Currently, the reactor's fuel elements are

181   composed of low enriched uranium (LEU), i.e., up to < 20 % enriched uranium (^{235}U

182   isotope), assembled as fuel plates of U_3Si_2 dispersed in Al. This fuel is manufactured in

183   IPEN's Nuclear Fuel Center, in sequential steps of the nuclear fuel cycle.

184

185   During the step of precipitation of uranium tetrafluoride (UF_4), the effluent is collected

186   and subjected to an initial treatment for prior removal of stannous ions (Sn^{2+}) and

187   fluoride ions (F^-), which are present at very high concentrations, about 50 g L^{-1} of Sn

188   and 56 g L^{-1} of F. This previous treatment involves sequential precipitation as $Sn(OH)_4$

189   and CaF_2, decreasing these species' concentrations in the effluent to acceptable

190   regulatory levels of < 4.0 μg L^{-1} for Sn and < 10.0 μg L^{-1} for F, according to Brazil's

191   National Council for the Environment, CONAMA (CONAMA, 2011). The first

192   precipitation step is performed by adding Na_2CO_3 to hydrolyze Sn as $Sn(OH)_4$. At this

193   step, part of the uranium is adsorbed on the precipitate because uranium forms a soluble

194   complex with the carbonate. In the second step, CaO is added for F removal as CaF_2

195   and U, in the form of uranyl fluoride (UO_2F_2), is concomitantly precipitated as calcium

196   diuranate (CaU_2O_7).

197

198   Although uranium gets partially removed in this two-step precipitation stage, a remnant

199   concentration of approx. 5 mg L^{-1} of uranium persists in solution, exceeding regulatory

200   levels (CNEN, 2014) and, therefore, it cannot be discharged into the environment as an

201   industrial effluent. The dispersion of radionuclides such as uranium in the aqueous

202   media (surface water and groundwater) can cause serious consequences linked to water

203   consumption. Radionuclides can be taken up and concentrated by aquatic plants and

204   animals, thereby posing a potential risk to animals higher in the food chain, including

205   humans. Also, the radionuclides can deposit in the bottom sediments and concentrate

206   over time, increasing their long term availability to bottom feeders. All of these can

207   have larger implications in particular ecosystems with consequent impacts in

208   biodiversity (IAEA, 2005).

209

210   To date, a variety of carbon-based adsorbents has been investigated for U removal from

211   wastewater including activated carbons (Abbasi and Streat, 1994; Kütahyalı and Eral,

212   2010; Mellah et al., 2006; Öter and Selçuk Zorer, 2019; Saputra et al., 2019) and

213   biochars (Dai et al., 2020; Guilhen et al., 2019a; Guilhen et al., 2019b; Hadjittofi and

214   Pashalidis, 2015; Zhang et al., 2013; Ding et al., 2018). Previous investigations have

215   demonstrated the efficiency of the non-activated macauba biochar in the removal of

216   uranium (Guilhen et al., 2018, 2019a; 2019b). However, since activated biochars have

217   previously indicated improved sorption capacities, the study of activated macauba

218   biochar for the removal of uranium is justified. To the best of our knowledge,

219   systematic investigations on the effects of physical activation on uranium removal from

220   aqueous solution using macauba endocarp-derived biochar are virtually inexistent in the

221   literature, despite the prevalence of this biomass in tropical regions of the Americas.

222　Macauba is used for production of oil and can also be used for production of biodiesel

223　(Rivera-Utrilla et al., 2011). As a result, large quantities of discarded endocarp

224　accumulate and can pose environmental problems. Identifying an effective use for this

225　material would therefore bring about not only environmental, but also economic

226　benefits (as a result of reduced demand for unsustainable and costly activated carbon).

227　According to our previous investigation (Guilhen et al., 2019b), the low-temperature

228　biochar, namely BC350, was identified as the most promising sorbent among those

229　assessed. Thus, this paper focuses on exploring further improvements that can be

230　achieved by doing the activation of this selected material.

2. MATERIALS AND METHODS

2.1. Materials

The endocarp from the macauba palm coconut was supplied by SOLEÁ BRASIL (João Pinheiro, MG, Brazil). A standard solution of 1000 mg L^{-1} of uranium was prepared through the dissolution of U_3O_8 certified reference material (CRM 129-A, natural ^{238}U), supplied by New Brunswick Laboratory (New Brunswick, NJ, USA). 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 (Merck, Darmstadt, HE, Germany).

2.2. Sample preparation

After an initial selection step for the removal of dirt and unbroken coconuts, the clean shells were ground in a cutting mill FA300 (Rone Ind. Com. De Máquinas Ltda., Carapicuíba, SP, Brazil) passing over a 3/8 mesh screen and subsequently air-dried at 100 ºC for 3 h.

2.3. Biochar production

A Thermo Fisher Scientific (Asheville, NC, USA), Lindberg Blue M, horizontal tubular steel reactor, with a heating range from 100 to 1100 °C, was used to perform the

254   pyrolysis (Fig. 1). The pyrolysis temperature was set by a central temperature controller

255   and a type K thermocouple was used as secondary control inside the reactor, in the same

256   heating zone where the sample was placed. The samples were placed in an alumina

257   vessel and inserted in the reactor's tube with 0.055 m internal diameter through water-

258   cooled flanges.

259

260   Before initiating the pyrolysis, the reactor was purged with argon (Ar) for 20 min. Once

261   the targeted temperature was adjusted, the heating took place under inert argon

262   atmosphere. The carbonized samples were denominated as "BCT", in which "T"

263   corresponds to the highest treatment temperature (HTT); for instance: BC350 is the

264   biochar obtained at the HTT of 350 ºC.

265

266   Approximately 30 g of dry endocarp was processed at a time, applying an argon gas

267   flow of 40 mL min^{-1} and a 5 °C min^{-1} heating rate. The sample was kept at a specific

268   HTT for 1 h (residence time). Finally, the cooled biochar was ground in a cutting mill

269   passing over a 120 mesh screen.

270

271   **2.4. Adsorption experiments**

272

273   Batch technique was used for the equilibrium adsorption experiments, which were

274   performed at room temperature (25 °C) in a rotary shaker MA140 (Marconi

275   Equipamentos para Laboratórios, Piracicaba, SP, Brazil) using 100 mL glass Beckers at

276   120 rpm stirring rate for 24 h. The adsorbent was separated by filtration using an SCP

277   Science 0.45 microns Teflon membrane filter (Baie-D'Urfé, QC, Canada) and the U(VI)

278   concentration in the reminiscent filtrate solution was determined using a Spectro

279   ARCOS ICP OES (Kleve, NRW, Germany).

280

281   The adsorption capacity (mg g^{-1}) of the adsorbent was calculated using Eq. (1):

282

$$q_t = \frac{(C_0 - C_t) \times V}{M} \qquad \qquad \text{Eq. (1)}$$

283

284   where "q_t" is the adsorbed amount of adsorbate per gram of adsorbent at any time "t",

285   "C_0" and "C_t" the concentrations of the adsorbate in the initial solution and at any time

286   "t", respectively (mg L^{-1}); "V" the volume of the adsorbate solution added (L) and "M"

287   the amount of the adsorbent used (g).

288

289   The extraction efficiency was determined through the following equation (Eq. (2)):

290

$$R\ (\%) = \left(\frac{C_o - C_t}{C_o} \right) \times 100 \qquad \qquad \text{Eq. (2)}$$

291

292   where "R" is the extraction efficiency or retention percentage, "C_0" (mg L^{-1}) is the

293   initial concentration of each adsorbate and "C_t" (mg L^{-1}) represents the concentration of

294   the adsorbate at time "t".

295

2.4.1. Adsorption using activated BC

Although BC350 performed very promisingly in the removal of uranium from aqueous solutions (Guilhen et al., 2019b), the remaining solution still exceeded regulatory levels (CNEN, 2014). In order to verify if activation enabled the improvement in the adsorption capacity of the macauba biochar, experiments were conducted, comparing both activated (BC350A) and non-activated biochar (BC350), considering various initial uranium concentrations.

To do so, independent duplicates with different U(VI) concentrations, ranging from 1 to 200 mg L^{-1}, were prepared in pH 3 and put in contact with a 10 g L^{-1} dosage of the adsorbents (BC350-A and BC350). The system was subjected to a 120 rpm stirring rate at room temperature for 24 h. These adsorption parameters have been previously established through experimentation and optimized for maximum uranium removal (Guilhen et al., 2019a).

2.5. Physical activation

The process of physical activation, also known as partial degasification (Contescu et al., 2018), was applied to the BC350. When CO_2 is used as activating agent, the activation equation can be described according to the reverse-Boudouard reaction:

$$C + CO_2 \rightleftharpoons 2CO \qquad\qquad\qquad Eq.\ (3)$$

318

319   $\Delta H \cong + 170$ kJ mol^{-1} at 298 K.

320

321   The reaction is endothermic, i.e., the product is higher in energy than the reactants.

322   Therefore, the change in enthalpy is positive and heat must be supplied to favor the

323   reaction. Temperatures above 700 °C are required to promote the reaction.

324

325   The activation was carried out by heating the BC350 up until 850 °C under Ar

326   atmosphere at a 10 °C min^{-1} heating rate. Once the sample reached 850 °C, the Ar

327   supply was interrupted and a 20 mL min^{-1} flow of CO_2 was introduced in the pyrolysis

328   reactor (Castro, 2009), replacing the Ar flow. The sample was kept under these

329   conditions for 2 h.

330

331   After activation, the sample was acid washed using 0.5 mol L^{-1} of HCl to remove

332   impurities from inside the pores, followed by subsequent washes with warm and cool

333   distilled water. The activated sample, denominated "BC350-A", was oven-dried at 110

334   °C and stored in a desiccator before further use.

335

336   **2.6. N₂ adsorption analysis**

337

338   The N_2 adsorption analysis at 77 K was performed using Micromeritics, TriStar II 3020

339   V1.03 (Norcross, GA, USA), surface, and porosity analyzer.

340

341   **2.7 Adsorption isotherm models**

342

343   Four isotherm models (Langmuir, Freundlich, Toth and Redlich-Peterson) were tested

344   for modeling the adsorption isotherms by nonlinear method. See the supplementary

345   material for further details on the isotherm models.

346

347   **2.8 Parameter estimation**

348   A "search method" called *Downhill Simplex* was used to optimize the parameters in

349   order to adjust the mathematical models that most accurately represent the observed

350   date. See the supplementary material for a full description of the method.

351

352   **2.9 Characterization**

353

354   Nitrogen adsorption analysis was used to characterize the biochar's specific surface area

355   and adsorption isotherms were obtained to assess the U(VI) adsorption onto the

356   activated biochar. Surface analysis was evaluated by Fourier-Transform infrared

357   spectroscopy (FTIR), the morphology of the activated and non-activated biochars was

358   observed by scanning electron microscopy (SEM) analysis and the presence of U(VI)

359   was detected by micro X-ray fluorescence spectrometry.

360

361 Surface analysis was carried out using a Perkin Elmer Spectrum One FTIR

362 spectrophotometer (PerkinElmer Inc., Waltham, USA). High-resolution imaging of both

363 activated and non-activated biochars were obtained using a FEI Quanta 650FEG

364 scanning electron microscope (FEI Company, Hillsboro, USA). A Shimadzu Micro X-

365 ray fluorescence spectrometer μ-EDX 1300 (Shimadzu Corporation, Kyoto, Japan) was

366 used to confirm the presence of uranium in the activated biochar. A Spectro ARCOS

367 inductively coupled plasma optical emission spectrometer (Spectro Analytical

368 Instruments Co., Kleve, Germany) and a Thermo iCAP inductively coupled plasma

369 mass spectrometer (Thermo Fisher Scientific, Waltham, USA) were employed for

370 multi-element analysis.

371

372 **2.10 Application in treatment of U(VI) effluent**

373

374 A multi-elemental analysis of the residual effluent, previously treated to remove Sn and

375 F, was performed in order to determine which other elements were present in such

376 amounts that could interfere or compete in the process of U(VI) adsorption. Also, the

377 residual effluent is alkaline (pH approx. 8) and a previous study with BC350 showed

378 that a better performance was achieved when U(VI) solution was adjusted to pH 3

379 (Guilhen et al., 2019a). The adsorption parameters have been optimized using the

380 biochar obtained at 350 °C (BC350), because it was the temperature at which the

381 gravimetric yield factor provided the best compromise between fixed carbon and

382 gravimetric yield (Guilhen et al., 2019b).

383

384   The removal of U(VI) from the aqueous pre-treated UF$_4$ effluent using BC350-A was

385   evaluated by testing three sub-samples, with solution pH values adjusted from 8 to 3

386   before addition of the adsorbent (Guilhen et al., 2019a). Inductively coupled plasma

387   mass spectrometry (ICP-MS) was used for the determination of the remaining U(VI) in

388   solution.

389

390   **3. RESULTS AND DISCUSSION**

391

392   **3.1. Activation**

393

394   Uranium adsorption onto BC350-A was evaluated for a wide range of solution

395   concentrations between 1 and 200 mg L^{-1}, adjusted to pH 3, using an adsorbent dosage

396   of 10 g L^{-1}. The results are shown in Fig. 2.

397

398   The uranium removal was significantly higher on the activated biochar (BC350-A),

399   achieving over 99 % removal for an initial concentration of 5 mg L^{-1}, whereas for the

400   non-activated biochar (BC350), the removal efficiency achieved was of 80.5 % at the

401   same initial concentration (Guilhen et al., 2019b). The average remaining concentration

402   of U(VI) was 0.041 mg L^{-1} (41 µg L^{-1}) and the final pH measured was 5.7. Additionally,

403   the removal efficiency was over 90 % and practically constant for a wider range of

404   concentrations (2.5 to 25 mg L^{-1}) when the activated BC was used.

405

406   The adsorption capacity (q) of BC350-A increased with increasing initial uranium

407   concentrations. At an initial uranium concentration of 5 mg L^{-1}, the adsorption capacity

408   was 422.0 mg g^{-1} for BC350 (Guilhen et al., 2019b) and 488.7 mg g^{-1} for BC350-A

409   (Table S3). The highest uranium adsorption capacity (q = 11,750 mg g^{-1}) in the range

410   investigated was achieved at an initial concentration of 200 mg L^{-1} when BC350-A was

411   used.

412

413   The BC350-A behavior can be explained in terms of exchangeable sites in the activated

414   adsorbent structure, evidencing that the activation process successfully increased the

415   adsorption sites in the biochar structure. According to Gulnaz et al. (2004), the initial

416   increase in the adsorbate's concentration will increase the driving force of the

417   concentration gradient, causing an increase in adsorption capacity.

418

419   As the ratio of uranium to BC350-A ($[U]/m_{BC350-A}$) increases, the exchangeable sites in

420   the BC structure get saturated, resulting in decreasing driving force and removal

421   efficiency. In contrast, the adsorption capacity increased with initial uranium

422   concentration (constant mass of adsorbent), which may be due to an increase in the

423   driving force of the concentration gradient as the initial adsorbate concentration

424   increased.

425

426   The adsorption capacity achieved for an initial uranium concentration of 5 mg L^{-1} (q_e =

427   488.7 mg g^{-1}) was used to compare the efficiency of BC350-A with other materials,

428   which have been previously tested as adsorbents for U(VI). When compared to other

429   organic, inorganic and biological adsorbents reported in literature, BC350-A is among

430   the highest performing adsorbents for U(VI) adsorption (Table S1).

431

432   **3.2 N$_2$ adsorption analysis**

433

434   N$_2$ adsorption analysis allowed the determination of the specific surface area (BET),

435   pore volume and mean pore size for the activated and non-activated biochar samples,

436   BC350-A and BC350, respectively. The results obtained are presented in Table S2.

437

438   As expected, the BET surface area increased with activation. Biochar activation took

439   place at 850 °C, 500 degrees higher than the pyrolytic temperature employed to produce

440   the BC350 sample. Surface area increased with increasing temperatures due to the

441   escape of volatile substances and the formation of channels in the biochar structure. The

442   porosity development is further promoted by the gasification process during physical

443   activation with CO_2. The activation results are consistent with what has been described

444   in the literature (Ahmad et al., 2012; Chen et al., 2012; Kim et al., 2013).

445

446   The N_2 adsorption-desorption isotherm for BC350 and BC350-A are shown in Fig. S1.

447   Type II-isotherm best fits the BC350, according to the IUPAC's classification (Martín-

448   Martínez, 1990; Thommes et al., 2015). Type II isotherms are observed for nonporous

449   or macroporous materials.

450

451   Generally, isotherms obtained for physically activated charcoals tend to correspond to

452   the Type IV, traditionally attributed to mesoporous solids with a significant

453   microporous fraction (Crini and Badot, 2011). However, the isotherm obtained for

454   BC350-A is compatible with Type I isotherms, according to the IUPAC's classification

455   (Thommes et al., 2015), which represent microporous solids.

456

457   Type I isotherms show a rapid increase in adsorbed gas pressure as pressure increases

458   until reaching a plateau. This is due to the great ease of adsorption in pores with

459   diameters smaller than 2 nm. After micropore filling, there are virtually no other regions

460   where adsorption is significant. The curve, therefore, exhibits an almost constant region

461   and grows back when condensation begins to take place (Teixeira et al., 2001).

462

463   The isotherm shown in Fig. S1 (BC350-A) exhibits a hysteresis cycle. The upward

464   curve represents the measurements obtained by progressive addition of the adsorbent

465   gas (adsorption) until saturation, while the downward curve represents the progressive

466   withdrawal (desorption) (Rouquerol et al., 1999). According to the IUPAC's

467   classification (Martín-Martínez, 1990), this cycle has the aspect of "H4", being

468   associated with narrow slit pores with wedge shapes, cones and/or parallel plates and

469   cylindrical capillaries open at both ends (Lowell et al., 2012; Sing, 1985; Thommes,

470   2010; Thommes et al., 2015, 2013).

471

472   It is also observed that for low relative pressure values (P/P$_0$ ≈ 0,1), the volume of N$_2$

473   adsorbed by BC350-A is 3×10^{-1} cm^3 g^{-1}, which is much higher compared to the volume

474   adsorbed by BC350 (1.4×10^{-3} cm^3 g^{-1}). This increase in adsorbed volume at low

475   relative pressures is due to a higher microporous development (< 2 nm), which leads to

476   a larger specific surface area in the BC350-A. When P/P$_0$ ≈ 1, the volume of adsorbed

477   gas is also higher for the activated sample and, in this case, this is related to the

478   maximum capacity of total gas adsorption by the solid, evidencing the highest porosity

479   in the activated biochar.

480

481   Pore size distribution for BC350 is shown in Fig. S2. A predominance of medium-sized

482   porous, characteristic of mesoporous materials (2 to 50 nm), with an average pore size

483   of 30 nm was observed. However, a significant macroporous fraction (> 50 nm) was

484   observed, which is consistent to the surface area of 0.83 m^2 g^{-1} (0.5 to 2 m^2 g^{-1}) as

485   shown in Table S2.

486

487   Pore size distribution for BC350-A is shown in Fig. S2. A prevalence of micropores can

488   be observed as a consequence of the physical activation, contributing to the increase of

489   micropore volume (Table S2). The average pore size of BC350-A was 2.9 nm and the

490   pore volume was 0.3 cm^3 g^{-1}, characterizing the activated material as essentially

491   microporous. Therefore, the isotherm data were adjusted by the t-plot method.

492

493   Comparison of the porous structure of activated and non-activated samples indicates

494   that the activation process clearly led to an increase in porosity of activated samples.

495   The porosity (P) of BC350-A was determined as the volume of voids in the biochar,

496   calculated according to Eq. (4):

497

$$P(\%) = \frac{(True\ density - Bulk\ density) \times 100\%}{True\ density} \qquad \text{Eq. (4)}$$

498

499   BC350-A's true (1.98 g cm^{-3}) and bulk densities (0.74 g cm^{-3}) were applied in Eq. (4)

500   and the calculated porosity (P) is approximately 63 %. Therefore, BC350-A can be

501   classified as a material of very high porosity (P > 50 %) (Fiori and Carmignani, 2001).

502

503   **3.3 Adsorption isotherms**

504

505   The results of the U adsorption on the activated biochar, BC350-A, are presented in

506   Table S3 and could be mathematically represented by isotherms. Langmuir, Freundlich,

507   Toth and Redlich-Peterson isotherms were employed in the study of the U/BC350-A

508   system. The obtained graphs are shown in Fig. 3.

509

510   The respective parameters, obtained by non-linear regression for each isotherm model,

511   are shown in Table 1.

512

513   **Table 1.** Experimental parameters of the adsorption isotherm models of the U/BC350-A

514   system.

Langmuir	Q_{max} (mg g^{-1})		K_L (L mg^{-1})		$R^2_{adj.}$
	107.08		2.12		0.883
Freundlich	K_F ((mg g^{-1})(mg L^{-1})$^{-1/nF}$)		n_F		$R^2_{adj.}$
	69.94		2.09		0.927
Toth	K_T (L mg^{-1})	a_T (L mg^{-1})	t		$R^2_{adj.}$
	2.22	0.47	0.02		0.872
R-P	K_{RP} (L g^{-1})	a_{RP} (mg L^{-1})$^{-\beta}$	β		$R^2_{adj.}$
	93.59	16.48	0.19		0.955

515

516   The highest degree of correlation, using Pearson's correlation coefficient (R^2), was

517   obtained for Freundlich and Redlich-Peterson adsorption isotherms at 0.93 and 0.95,

518   respectively, compared to Langmuir and Toth adsorption isotherms (0.88 and 0.87,

519   respectively).

520

521   However, the R^2 values for Freundlich and Redlich-Peterson are very close to each

522   other, making it difficult to use this parameter as a selection criterion. Thus, an estimate

523   of the best fit for the isotherm model was performed by calculating different equations

524   for deviation estimate, also called "error functions" (Foo and Hameed, 2010) as shown

525   in Table S4.

526

527   Since mathematical models are only an attempt to describe reality (Ncibi, 2008), the

528   deviation estimates are better suited to obtain a more accurate fit. The deviation

529   estimates, shown in Table S4, compare the experimental q_e (q_{eexp}), described in Table

530   S3, with the calculated q_e (q_{ecalc}) using the equations shown in Table S4. The lower

531   values of these estimates indicate the best fitting isotherms.

532

533   The most suitable model for satisfactorily describing the adsorption phenomenon of the

534   U/BC350-A system is based on the highest determination coefficient (R^2) and the

535   lowest values of RAE, SSR, MPSD, HYBRID, SAE and X^2 altogether.

536

537   As can be seen in Table S5, the Redlich-Peterson model provided the best fit of the

538   experimental data, suggesting heterogeneity of adsorption sites (Olivelli et al., 2013),

539   with different affinities for uranium, or the existence of a cooperative effect (Hinz,

540   2001), which increases the affinity between uranyl ions and adsorption sites.

541

542   Since the Redlich-Peterson equation is a hybrid isotherm, that incorporates

543   functionalities of both the Langmuir and the Freundlich isotherms (Foo and Hameed,

544   2010), it was expected that the fit of the experimental data for this equation would be

545   better than that obtained with the Langmuir and Freundlich equations. The modeling

546   reveals, thus, a hybrid adsorption mechanism.

547

548   This supports previous findings in recent literature. For instance, Li et al. (2019)

549   employed biochar derived from *Ficus microcarpa* aerial root and also compared raw

550   and modified biochar. Their findings also indicated the Redlich-Peterson to be the best

551   fitting isotherm for both biochars ($R^2 = 0.96$ for raw biochar, $R^2 = 0.98$ for modified

552   biochar). Another example is the work of Vieira et al. (2019), who studied the

553   adsorption of U(VI) onto macrophytes. For *Pistia stratiotes*, the Redlich-Peterson

554   equation provided the best fit for the experimental data ($R^2 = 0.86$, corrected Akaike

555   information criterion = -175.2).

556

557   **3.4 Characterization**

558

559   A comparison of FTIR spectra of BC350 and BC350-A is shown in Fig. 4. The FTIR

560   spectra for BC350 have been already discussed in a previous study (Guilhen et al.,

561   2019b) and Fig. 4 contrasts it against that of activated biochar.

562

563   The absorption bands attributed to the −OH stretching of hydroxyl and carboxylic acid

564   groups (3600–3300 cm^{-1}) and to the C=C stretching of aromatic structures (1650–1520

565   cm^{-1}), that are practically non-existent in the BC350-A spectrum, are much more

566   pronounced in the BC350 spectrum. Previous findings (Guilhen et al., 2019b) showed

567   that the uranyl ions were adsorbed onto BC350 by chemisorption, enabled by hydroxyl

568   and carboxylic acid surface groups. Other bands corresponding to the –CH$_2$ and –CH$_3$

569   stretching of aliphatic chains (2942 cm^{-1}) and aromatic –CO and phenolic –OH at 1270

570   cm^{-1} were also considerably reduced in the BC350-A sample.

571

572   These spectra are in agreement with previous observations (Guilhen et al., 2019b) and

573   are the result of the process of thermal decomposition, in which the increase in the

574   pyrolytic temperature causes loss of surface functional groups and subsequent decrease

575   in acidity and polarity of the surface (Kim et al., 2013), indicating that physisorption is

576   the ruling mechanism of adsorption in the U/BC350-A system and was enabled because

577   of the increased specific surface area of the BC350-A.

578

579   The micrographs shown in Figs. 5 and 6 correspond to the topography images of the

580   BC350 and BC350-A, respectively.

581

582   Despite the high heterogeneity of the surfaces, the morphology of BC350 is very

583   characteristic of chars, with porous cavities and intertwined channels formed by the

584   transport of water vapor and volatiles to the surface of the material (Bandosz, 2006).

585

586   In the micrographs of BC350-A (shown in Fig. 6) it is possible to observe a morphology

587   that is characteristic of activated chars. The release of volatile components promoted the

588   formation of a structure with vascular bundles or channels that provide greater

589   permeability to the material due to the increased surface area.

590

591   These microscopic images evidence the role of activation in removing residues that

592   remained from the biomass decomposition and the volatilization of bituminous

593   substances and tars during the process of carbonization, in which rudimentary pores are

594   already created. On physical activation, these residues react with the flow of gases (in

595   this case, CO_2) at elevated temperatures (850 °C), getting oxidized. As a result, the pre-

596   existing pores get cleared and widened (because CO_2 oxidizes the carbonaceous

597   material present inside the pores as well), increasing the surface area. An increased

598   surface area exposes more surface groups, favoring chemical and physical interactions

599   with uranyl ions.

600

601   Energy-dispersive micro X-ray fluorescence spectrometry (Micro-XRF) was employed

602   to detect the presence of adsorbed uranium in BC350-A. This technique was selected

603   over the conventional XRF because of its sensitivity, capable of detecting uranium in

604   lower concentrations. Therefore, this technique provides evidence that the uranium was

605   actually absorbed onto BC350-A. The results are shown in Table S6.

606

607   The characteristic X-rays emitted by the innermost layers of a given element are

608   grouped under the name K_α and K_β, resulting from electronic transitions $L \rightarrow K$ and M

609      $\rightarrow K$, respectively (Lyman series). Similarly, the characteristic X-ray emission lines L_α

610   and L_β originate from the electronic transition of the layers M → L ($L_{\alpha 1}$, $L_{\alpha 2}$ e $L_{\beta 1}$) and

611   N → L ($L_{\beta 2}$) (Balmer series) (Khoury Asfora, 2010).

612

613   The emission line K_α characteristic of "Fe" has a very low intensity, indicating its

614   presence as a probable impurity in the material. The K_α and $K_{\alpha C}$ (Compton) lines of Rh

615   are due to the Rh tube (the X-ray source).

616

617   Exposure of the sample to the X-ray beam promotes the excitation of the L layers in the

618   adsorbed U. The β transition lines of U (16.48 keV and 17.23 keV) are the least likely to

619   occur and have higher energy than the α transition line (13.66 keV). The indices "1" and

620   "2" in the transitions $L_{\beta 1}$ and $L_{\beta 2}$ indicate the transition between the sublayers M-IV →

621   L-II and N-V → L-III. The most intense transition occurs in L_α. Since uranium has

622   electrons distributed in layers of orders higher than M, it is also possible to identify a

623   transition U M_β referring to the transition N-V (O) → N-3 (M) (Paschen series).

624

625   Micro-XRF analysis provided an efficient way to identify the U present in the

626   adsorbent, thus proving the effective adsorption onto BC350-A.

627

628   **3.5 Application in UF₄ effluent treatment**

629

630   As can be seen in Table 2, the sequential initial treatment reduced the concentration of

631   Sn and F species in solution to values lower than the allowable limits according to the

632   Resolution nº 430 of the Brazilian National Council for the Environment, CONAMA

633   (CONAMA, 2011).

634

635   **Table 2.** Sn, U and F levels after the pre-treatment in the Nuclear Fuel Center.

Element ($\mu g\ mL^{-1}$)	Effluent (Initial)	Effluent (Final)	Maximum levels	Regulatory Agency
Sn	$5 \times 10^4 \pm 1.6 \times 10^2$	< LOD	4	CONAMA (2011)
U	$7.6 \times 10^1 \pm 3 \times 10^{-1}$	5.1 ± 0.6	2.2×10^{-1}	CNEN (2014)
F	$5.6 \times 10^4 \pm 1.4 \times 10^2$	5.7 ± 0.5	10	CONAMA (2011)

636   *LOD = 0.5 $\mu g\ mL^{-1}$

637

638   However, CONAMA's Resolution Nº 430 (CONAMA, 2011) does not include the

639   maximum values for U release. Therefore, the liberation of effluents containing U must

640   comply with CNEN's resolution CNEN-NN-8.01 (CNEN, 2014), for which the

641   maximum limit for the mixture of U isotopes in the UF_4 effluent (80.25 % for ^{238}U and

642   19.75 % ^{235}U isotopic ratio) was calculated according to their respective specific

643   activities, considering an allowable discharge level of 5.6 kBq m^{-3} for both isotopes (see

644   section 3.5 of the supplementary Material).

645   According to the results presented in Table 2, the two-step treatment resulted in a

646   solution in which the remaining U concentration was 5 mg L^{-1}, therefore, not efficient

647   enough to comply with the regulatory demands (CNEN, 2014).

648

649 A complementary treatment of this solution, initially at pH 8, was performed using the

650 activated biochar (BC350-A) and the pH of the solution was adjusted to 3. After

651 adsorption, the remaining U concentration in solution was 1.1×10^{-1} µg mL^{-1} (2.8 kBq

652 m^{-3}) The presence of Na$^+$ ions in the solution (2.7×10^3 µg mL^{-1}) has likely influenced

653 the adsorption process, decreasing the removal efficiency initially achieved for the

654 aqueous solution (Na$^+$ free) from 99.2% (4.1×10^{-2} µg mL^{-1}) to 97.9% (1.1×10^{-1} µg

655 mL^{-1}). Other elements such as Mg, B, Zn, Ni, As, Cu, Ba, Cr, Pb, Mn, Se, Fe, Cd and

656 Ag were also determined in the UF$_4$ effluent by ICP OES, but none of them scored

657 higher than 1×10^{-1} µg mL^{-1}, therefore, their influence were considered negligible

658 regarding coexistence interactions. Moreover, the U concentration in the treated solution

659 was below the maximum allowable limits of 5.6 kBq m^{-3} (CNEN, 2014).

660

661 **4. CONCLUSION**

662

663 CO_2 physical activation significantly enhanced the adsorption capacity of macauba

664 endocarp-derived biochar for uranyl ions in aqueous solutions, achieving over 99 %

665 removal for an initial concentration of 5 mg L^{-1}. The activation process led to an

666 increase in porosity with a specific surface area increasing from 0.83 to 643 m^2 g^{-1}.

667 Chemical surface of the biochar was significantly affected by activation. According to

668 the FTIR analysis, the activation process increased the aromaticity of the biochar,

669 indicating that the uranium adsorption was carried out by physical interactions. The

670 adsorption of uranyl ions onto the activated biochar was confirmed by µ-EDX analysis.

671 The Redlich-Peterson three-parameter equation isotherm model was the most

672 appropriate for fitting the experimental data, suggesting heterogeneity of adsorption

673 sites with different affinities for uranium setting up as a hybrid adsorption mechanism.

674 Finally, treating an actual U-containing effluent with BC350-A has proven to be

675 efficient in meeting the regulatory requirements. This study has therefore shown that an

676 ubiquitous low-cost biomass material such as macauba palm endocarp can be

677 successfully converted to activated biochar and used in treatment of industrial effluents,

678 specifically those containing uranyl ions.

679

687

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884 **Figure Captions**

885 **Fig. 1**. Scheme of the biochar/activated biochar production apparatus.

886 **Fig. 2**. Removal efficiency (a) and adsorption capacity (b) for BC350 and BC350-A.

887 **Fig. 3**. Adsorption isotherms of the U onto BC350-A.

888 **Fig. 4.** FTIR/UATR vibrational spectrum of BC350 and BC350-A.

889 **Fig. 5.** BC350 micrographs obtained by SEM in different magnifications.

890 **Fig. 6.** BC350-A micrographs obtained by SEM in different magnifications.