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1 **URANIUM REMOVAL FROM AQUEOUS SOLUTION USING MACAUBA**
2 **ENDOCARP-DERIVED BIOCHAR: EFFECT OF PHYSICAL ACTIVATION**

3

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17 **ABSTRACT**

18 The main aim of this study was to evaluate options for addressing two pressing
19 challenges related to environmental quality and circular economy stemming from
20 wastage or underutilization of abundant biomass residue resources and contamination of
21 water by industrial effluents. In this study we focused on residues (endocarp) from
22 Macaúba palm (*Acrocomia aculeata*) used for oil production, its conversion to activated
23 biochar, and its potential use in uranium (U) removal from aqueous solutions. Batch
24 adsorption experiments showed a much higher uranyl ions (U(VI)) removal efficiency
25 of activated biochar compared to untreated biochar. As a result of activation, an increase
26 in removal efficiency from 80.5 % (untreated biochar) to 99.2 % (after activation) was
27 observed for a 5 mg L⁻¹ initial U(VI) concentration solution adjusted to pH 3 using a 10
28 g L⁻¹ adsorbent dosage. The BET surface area increased from 0.83 to 643 m² g⁻¹ with
29 activation. Surface topography of the activated biochar showed a very characteristic
30 morphology with high porosity. Activation significantly affected chemical surface of
31 the biochar. FTIR analysis indicated that U(VI) was removed by physisorption from the
32 aqueous solution. The adsorbed U(VI) was detected by micro X-ray fluorescence
33 technique. Adsorption isotherms were employed to represent the results of the U
34 adsorption onto the activated biochar. An estimation of the best fit was performed by
35 calculating different deviation equations, also called error functions. The Redlich-
36 Peterson isotherm model was the most appropriate for fitting the experimental data,
37 suggesting heterogeneity of adsorption sites with different affinities for uranium setting
38 up as a hybrid adsorption. These results demonstrated that physical activation
39 significantly increases the adsorption capacity of macauba endocarp-derived biochar for
40 uranium in aqueous solutions, and therefore open up a potential new application for this
41 type of waste-derived biochar.

42

43

44 Keywords: biochar, activation, macauba, endocarp, uranium.

45

46

47 Main finding of the work:

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

51

52 1. INTRODUCTION

53

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

67

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

75

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, H₂, CO₂ and CH₄) 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 H₃PO₄, HNO₃, ZnCl₂, H₂SO₄, 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 $700\text{-}1000 \text{ }^\circ\text{C}$ 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 CO₂ 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 CO₂** 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 m²
170 g⁻¹ (Yang, 2013).

171

172 Water molecules are much smaller than CO₂ 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 CO₂
175 activation essentially forms and widens micropores (Dalai and Azargohar, 2007; Feng
176 et al., 2018). Also, CO₂ 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 (²³⁵U
182 isotope), assembled as fuel plates of U₃Si₂ 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 (UF₄), the effluent is collected
186 and subjected to an initial treatment for prior removal of stannous ions (Sn²⁺) 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 CaF₂, 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 Na₂CO₃ 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 CaF₂
195 and U, in the form of uranyl fluoride (UO₂F₂), is concomitantly precipitated as calcium
196 diuranate (CaU₂O₇).

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.

231 2. MATERIALS AND METHODS

232

233 2.1. Materials

234

235 The endocarp from the macauba palm coconut was supplied by SOLEÁ BRASIL (João
236 Pinheiro, MG, Brazil). A standard solution of 1000 mg L⁻¹ of uranium was prepared
237 through the dissolution of U₃O₈ certified reference material (CRM 129-A, natural ²³⁸U),
238 supplied by New Brunswick Laboratory (New Brunswick, NJ, USA). This solution was
239 used to prepare both adsorption and calibration solutions. All solutions were prepared
240 with ultrapure water (18.2 MΩ cm resistivity) and analytical grade nitric acid (Merck,
241 Darmstadt, HE, Germany).

242

243 2.2. Sample preparation

244

245 After an initial selection step for the removal of dirt and unbroken coconuts, the clean
246 shells were ground in a cutting mill FA300 (Rone Ind. Com. De Máquinas Ltda.,
247 Carapicuíba, SP, Brazil) passing over a 3/8 mesh screen and subsequently air-dried at
248 100 °C for 3 h.

249

250 2.3. Biochar production

251

252 A Thermo Fisher Scientific (Asheville, NC, USA), Lindberg Blue M, horizontal tubular
253 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 °C.

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

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

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

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

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

296 **2.4.1. Adsorption using activated BC**

297

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

304

305 To do so, independent duplicates with different U(VI) concentrations, ranging from 1 to
306 200 mg L⁻¹, were prepared in pH 3 and put in contact with a 10 g L⁻¹ dosage of the
307 adsorbents (BC350-A and BC350). The system was subjected to a 120 rpm stirring rate
308 at room temperature for 24 h. These adsorption parameters have been previously
309 established through experimentation and optimized for maximum uranium removal
310 (Guilhen et al., 2019a).

311

312 **2.5. Physical activation**

313

314 The process of physical activation, also known as partial degasification (Contescu et al.,
315 2018), was applied to the BC350. When CO₂ is used as activating agent, the activation
316 equation can be described according to the reverse-Boudouard reaction:

317



318

319 $\Delta H \cong + 170 \text{ kJ mol}^{-1}$ 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 Ar327 supply was interrupted and a 20 mL min⁻¹ flow of CO₂ 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 N₂ 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 data. 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 UF₄ 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 N₂ adsorption analysis**

433

434 N₂ 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 CO₂. 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 N₂ 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 ($P/P_0 \approx 0,1$), the volume of N_2
473 adsorbed by BC350-A is $3 \times 10^{-1} \text{ cm}^3 \text{ g}^{-1}$, which is much higher compared to the volume
474 adsorbed by BC350 ($1.4 \times 10^{-3} \text{ cm}^3 \text{ g}^{-1}$). This increase in adsorbed volume at low
475 relative pressures is due to a higher microporous development ($< 2 \text{ nm}$), which leads to
476 a larger specific surface area in the BC350-A. When $P/P_0 \approx 1$, 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 ($> 50 \text{ nm}$) was

484 observed, which is consistent to the surface area of $0.83 \text{ m}^2 \text{ g}^{-1}$ (0.5 to $2 \text{ m}^2 \text{ g}^{-1}$) 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 $0.3 \text{ cm}^3 \text{ g}^{-1}$, 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

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

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)		$R^2_{\text{adj.}}$
	107.08	2.12		0.883
Freundlich	K_F ((mg g ⁻¹)(mg L ⁻¹) ^{-1/n_F})	n_F		$R^2_{\text{adj.}}$
	69.94	2.09		0.927
Toth	K_T (L mg ⁻¹)	a_T (L mg ⁻¹)	t	$R^2_{\text{adj.}}$
	2.22	0.47	0.02	0.872
R-P	K_{RP} (L g ⁻¹)	a_{RP} (mg L ⁻¹) ^{-β}	β	$R^2_{\text{adj.}}$
	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_{exp}), described in Table
530 S3, with the calculated q_e (q_{calc}) 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 –CH₂ and –CH₃
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, CO₂) at elevated temperatures (850 °C), getting oxidized. As a result, the pre-
596 existing pores get cleared and widened (because CO₂ 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 → K and M
609 → 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 $M \rightarrow L$ ($L_{\alpha 1}$, $L_{\alpha 2}$ e $L_{\beta 1}$) and
611 $N \rightarrow L$ ($L_{\beta 2}$) (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 $M-IV \rightarrow$
621 $L-II$ and $N-V \rightarrow L-III$. 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 $U M_{\beta}$ referring to the transition $N-V (O) \rightarrow N-3 (M)$ (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 n° 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 ($\mu\text{g mL}^{-1}$)	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 = $0.5 \mu\text{g mL}^{-1}$

637

638 However, CONAMA's Resolution N° 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 UF₄ effluent (80.25 % for ²³⁸U and
642 19.75 % ²³⁵U 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 $1.1 \times 10^{-1} \mu\text{g mL}^{-1}$ (2.8 kBq
652 m^{-3}) The presence of Na^+ ions in the solution ($2.7 \times 10^3 \mu\text{g mL}^{-1}$) has likely influenced
653 the adsorption process, decreasing the removal efficiency initially achieved for the
654 aqueous solution (Na^+ free) from 99.2% ($4.1 \times 10^{-2} \mu\text{g mL}^{-1}$) to 97.9% ($1.1 \times 10^{-1} \mu\text{g}$
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 $1 \times 10^{-1} \mu\text{g mL}^{-1}$, 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 $643 \text{ m}^2 \text{ g}^{-1}$.
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

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681

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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.