Activation Of Biochar Obtained From Slow Pyrolysis Of The Macauba Coconut Residue For Removing Uranium From Aqueous Solutions

Guilhen, S. N.; Ortiz*, N.; Izidoro, J. C.; Fungaro, D. A.

Chemistry and Environment Center
Nuclear and Energy Research Institute - IPEN
National Nuclear Energy Commission - CNEN
São Paulo – Brazil

*nortiz@ipen.br
Problem: Radioactive wastes

• Various activities in the nuclear industry (mining, research, fuel cycle, nuclear medicine) generate aqueous wastes containing radionuclides;

• Reduce the release of radioactive and toxic substances in the environment requires constant improvement of processes and technologies for treatment and conditioning of these wastes;

• Treatment of liquid radioactive wastes involves the application of several steps, such as filtration, precipitation, sorption, ion exchange, evaporation and/or membrane separation;

• It must meet the requirements for both – the release of decontaminated effluents into the environment and the conditioning of waste concentrates for permanent disposal;
Problem: Radioactive wastes

- Natural uranium is a mixture of 3 isotopes $^{234}\text{U} (0.005\%), \; ^{235}\text{U} (0.711\%)$ e $^{238}\text{U} (99.284\%)$, among which the most abundant is the U-238, with a half-life of 4.5 billion years;

- Chemically, they behave the same way;

- However, the U isotopes decay through alpha-particle emission in order to reach stability;

- Alpha particles are highly ionizing (cause damage to living tissues), although little penetrating;

- When ingested or inhaled, uranium particles can irradiate a person from the inside;
Problem: Radioactive wastes

- The **nuclear fuel cycle involves a series of steps in which several uranium compounds are generated**;

- IPEN’s research reactor uses a 19.75% enriched uranium fuel of uranium silicide \( U_3Si_2 \);

- One of the steps of the nuclear fuel cycle generates an **aqueous waste containing uranium** (uranium tetrafluoride effluent, \( UF_4 \)) at concentrations that are approximately 400 x higher than the maximum allowed limit;

- Standards in Brazil (regulated by CNEN) establish a maximum of 0.2 mg of U/L (200 ppb) in the wastewater, considering an enrichment degree of 19.75%.
Problem: Radioactive wastes

• A preliminary treatment step is performed through precipitation of U as sodium or ammonium diuranate;

• However, this process is not 100% effective and reminiscent ions remain in the solution – usually at concentrations still above the maximum established limits;

• Treatment of low concentrated solutions require a more refined technique – Adsorption is a simple and cost-effective technique, with the ability to specifically remove undesired substances from solutions;

• Several adsorbent materials are available: Biochars can be a good adsorbents for heavy metals because of their porous structure, charged surface, and surface functional groups. Moreover, they can be produced from natural renewable feedstocks.
Palm tree of high prevalence in Brazil, with potential to be produced in so-called silvopastoral systems without land use change and in an economically and socially sustainable way.

It has great economic potential. Its fruits/coconuts can be processed into plant oil destined for food and cosmetic industries as well as for the production of biodiesel and biokerosene; and animal fodder (press cake).

Endocarp = approx. 33% of the whole fruit
Biochar production

1. Remove dirt and unbroken coconuts.
2. Dried at 100°C for 3 hours.
3. Dried Endocarp.
4. Weighted alumina crucible, 30g each time.
6. Argon flow 40mL/min.
Fixed carbon yield

**Fixed Carbon Yield vs Temperature**

\[ FCY(\%) = BY(\%) \times FC(\%) \]
Adsorption parameters

**MACAUBA ENDOCARP**

**PYROLYSIS**

**MACAUBA BIOCHAR**

**BATCH EXPERIMENTS**

- **pH**
- **Dose**
- **C0**

**SHAKER**

- 120 rpm
- 25°C

**FILTRATION**

**U DETERMINATION ICP OES**

- Contact time: 3 hours
- Initial U Concentration: 5 mg/L
- Adsorbent Dose: 10 g/L
- Solution pH: 3

**BC350**

**q_t = \left(\frac{C_0 - C_t}{M}\right) \times V**

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

**pH = 2, 3, 4, 5, 6, 7**

**Dose = 1 - 20 g/L**

**C0 = 1 - 50 mg/L**
Adsorption experiments

Pyrolysis Temperature Effect

- q
- R

Pyrolysis Temperature (°C):
- 200
- 300
- 400
- 500
- 600
- 700
- 800

q (mg/g):
- 0
- 50
- 100
- 150
- 200
- 250
- 300
- 350
- 400
- 450

R (%):
- 0
- 20
- 40
- 60
- 80
- 100
Physical Activation

- Physical activation: gaseification process at 850°C using CO₂ atmosphere.
- BC350: non-activated biochar
- BC350-A: activated biochar

<table>
<thead>
<tr>
<th>Parameters</th>
<th>ASE (m² g⁻¹)</th>
<th>V_p (cm³ g⁻¹)</th>
<th>l_BET (Å)</th>
<th>l_BET (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC</td>
<td>643.12</td>
<td>0.298</td>
<td>30.45</td>
<td>3.04</td>
</tr>
<tr>
<td>BC350</td>
<td>0.8320</td>
<td>0.001295</td>
<td>383.181</td>
<td>38.31</td>
</tr>
</tbody>
</table>

ASE = specific superficial area; V_p = pore volume; l_BET = pore size
Results - Activation effect

For a $C_i = 5$ mg/L, the removal efficiency ($R$) is above 99% ($C_f = 41$ mg/L);

- $q_{\text{max}} = 489$ mg/g

- Encompassing concentrations from 2.5 to 25 mg/L.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>$q_{\text{max}}$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemically and thermally modified bentonite</td>
<td>29</td>
<td>Tsuruta, 2002</td>
</tr>
<tr>
<td>Conventional activated carbon</td>
<td>45</td>
<td>Morsy &amp; Hussein, 2011</td>
</tr>
<tr>
<td><em>E. canadensis</em></td>
<td>89</td>
<td>Yi <em>et al.</em>, 2016</td>
</tr>
<tr>
<td>Thermally treated carbon microspheres</td>
<td>92</td>
<td>Zhang <em>et al.</em>, 2013</td>
</tr>
</tbody>
</table>
Results – Adsorption Isotherms

<table>
<thead>
<tr>
<th>Model</th>
<th>R²</th>
<th>ARE</th>
<th>SSE</th>
<th>MPSD</th>
<th>HYBRID</th>
<th>SAE</th>
<th>X²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>0.972</td>
<td>6.10E+01</td>
<td>1.73E+07</td>
<td>2.70E+03</td>
<td>7.27E+04</td>
<td>1.24E+04</td>
<td>1.76E+05</td>
</tr>
<tr>
<td>Freundlich</td>
<td>0.968</td>
<td>8.91E+01</td>
<td>1.08E+07</td>
<td>2.40E+03</td>
<td>5.78E+04</td>
<td>1.03E+04</td>
<td>7.28E+03</td>
</tr>
<tr>
<td>Toth</td>
<td>0.968</td>
<td>7.47E+01</td>
<td>1.08E+07</td>
<td>2.51E+03</td>
<td>6.32E+04</td>
<td>1.03E+04</td>
<td>7.26E+03</td>
</tr>
<tr>
<td>R-P</td>
<td>0.974</td>
<td>3.99E+01</td>
<td>1.15E+07</td>
<td>2.32E+03</td>
<td>5.39E+04</td>
<td>1.04E+04</td>
<td>1.02E+04</td>
</tr>
</tbody>
</table>
Real case application

<table>
<thead>
<tr>
<th></th>
<th>Concentration (mg L$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UF$_4$ effluent initially generated</td>
<td>76.3</td>
</tr>
<tr>
<td>UF$_4$ effluent after preliminary treatment</td>
<td>5.1</td>
</tr>
<tr>
<td>UF$_4$ effluent after treatment using BC350-A</td>
<td>0.107</td>
</tr>
<tr>
<td>Maximum allowable limit (CNEN-NN-8.01)</td>
<td>0.217</td>
</tr>
</tbody>
</table>

- Treating the uranium-contaminated aqueous waste with the activated macauba biochar was successful.
Conclusions

• Non-activated biochar (BC350) achieved a removal of 80.1% for U(VI);

• Physical activation greatly improved BC350’s adsorption capacity, having achieved an adsorption capacity of 489 mg g⁻¹ for U(VI);

• Compared to other adsorbents in the literature, macauba’s biochar presented a better performance;

• Experimental data showed a better fit to the Redlich-Peterson model, indicating a hybrid adsorption mechanism;

• Macauba biochar proved to be a suitable adsorbent for the removal of uranium: a removal above 99% was achieved when BC350-A was used and the discharge levels were achieved;

• Real waste application successfully met the standards.
Special thanks to: