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

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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}U (0,005%), ^{235}U (0,711%) e ^{238}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 alfa-particle emission** in order to reach stability;
- **Alfa 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 tretrafluoride 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;

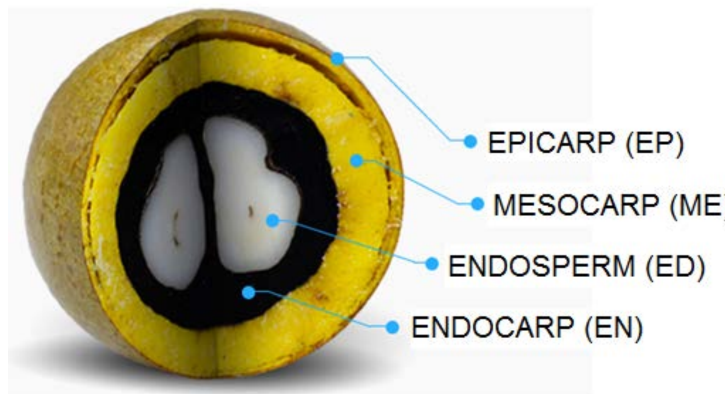
- Treatment of low concentrated solutions require a more refined technique – Adsorption is a simple and cost-effective technique, with the ability to specifically remove undesired substances from solutions;

- 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.**

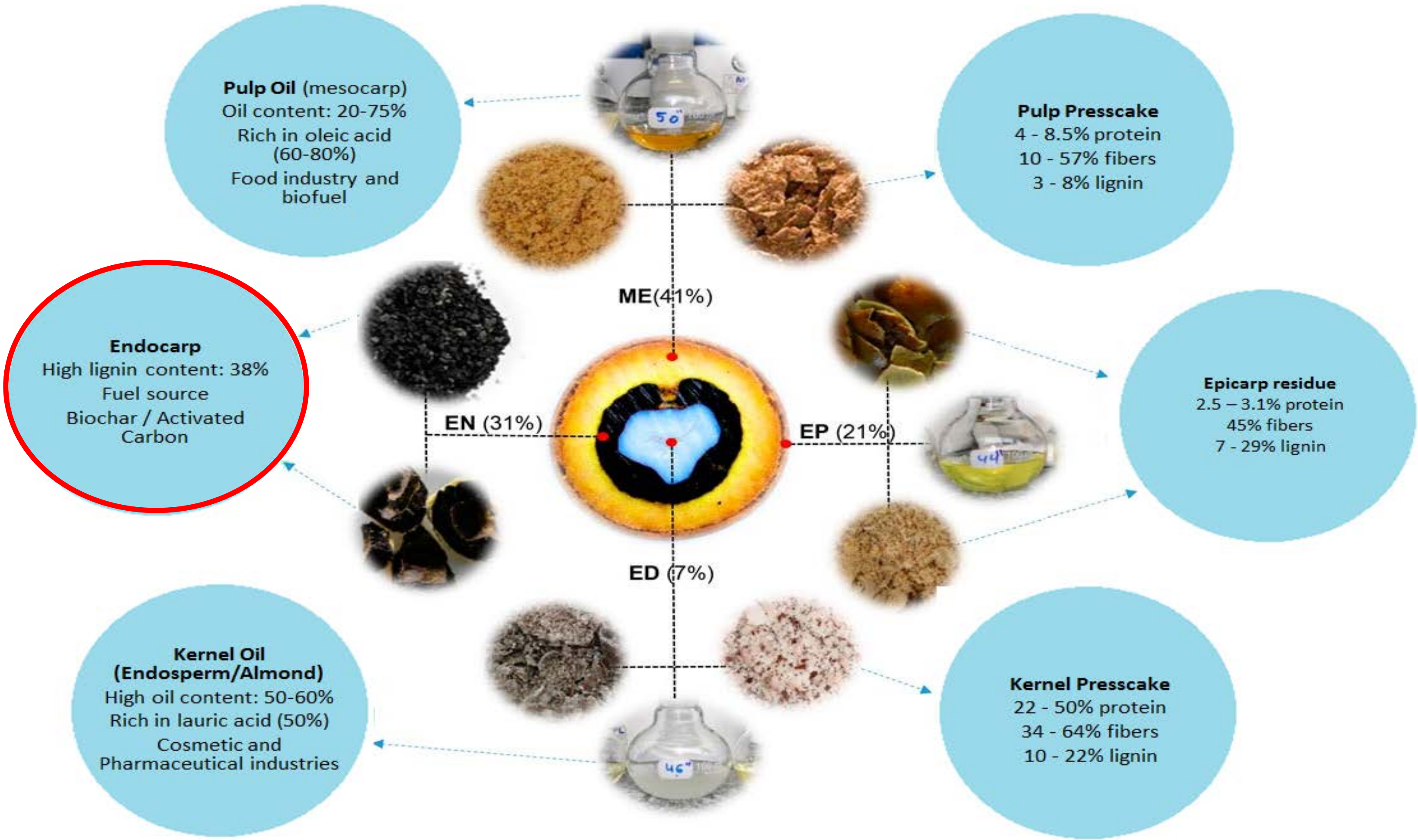
Macauba Palm Tree
(*Acrocomia aculeta*)

Palm tree of high prevalence in Brazil, with potential to be produced in so-called silvopastoral systems without land use change and in na ecomically 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 biodielsel and biokerosene; and animal fodder (press cake).

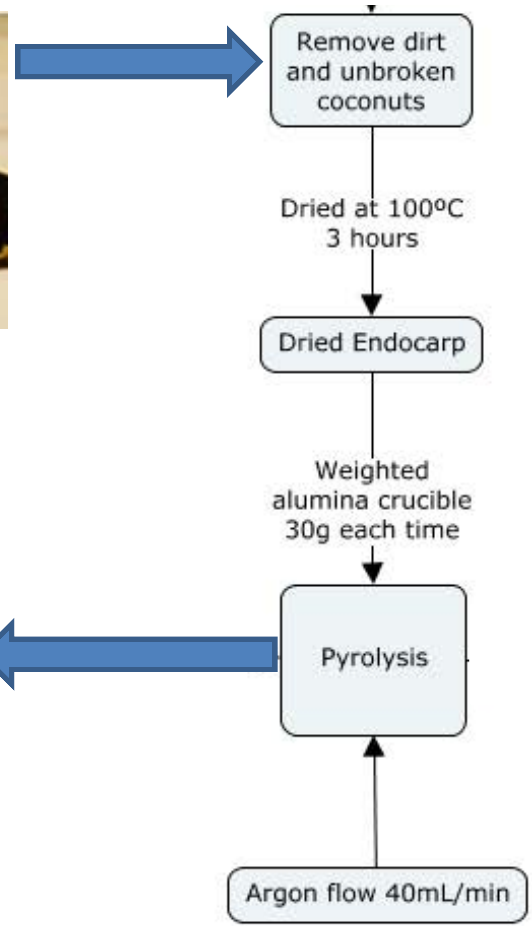


Endocarp = approx. 33% of the whole fruit



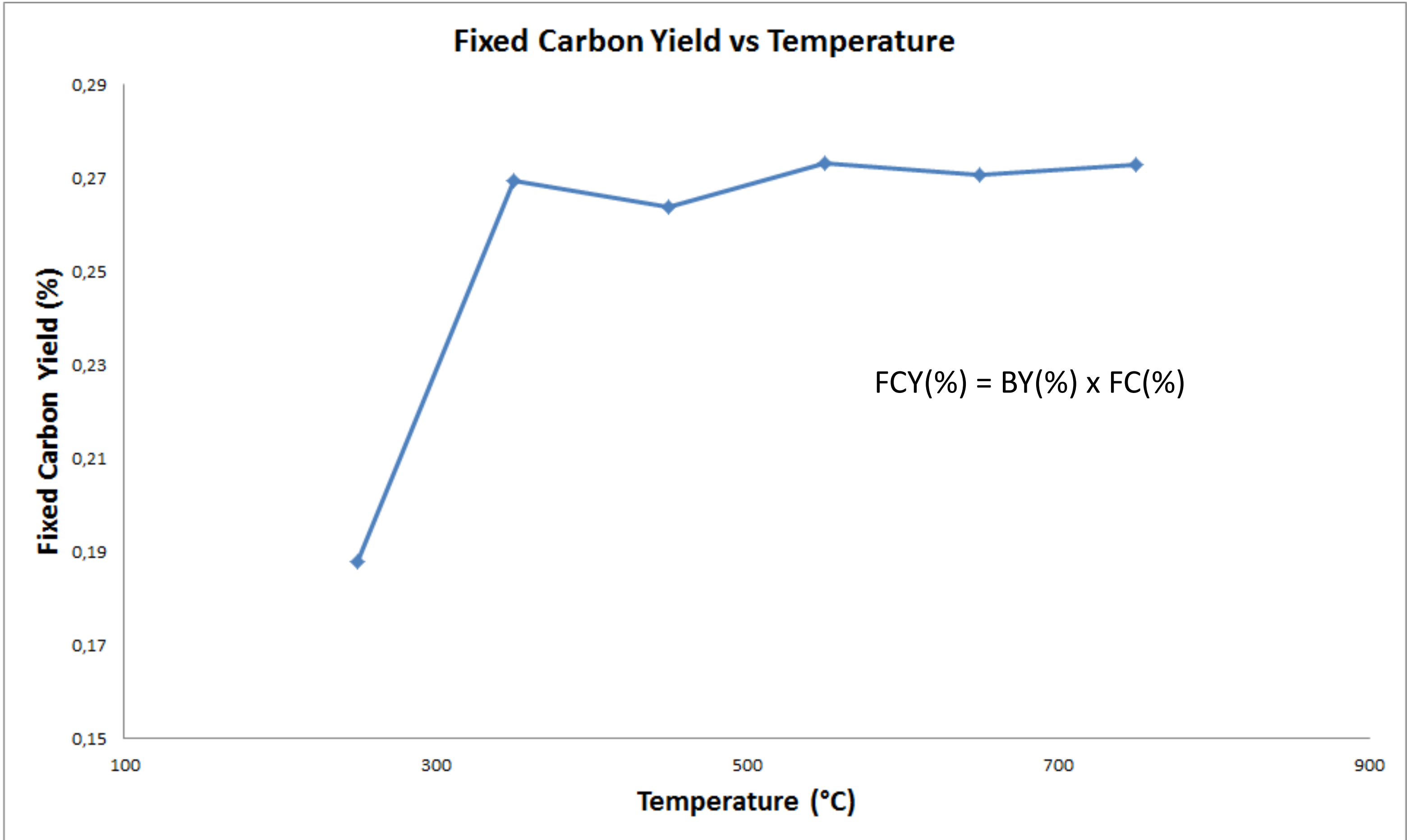
Pulp Oil (mesocarp)
Oil content: 20-75%
Rich in oleic acid (60-80%)
Food industry and biofuel
Pulp Presscake
4 - 8.5% protein
10 - 57% fibers
3 - 8% lignin
Endocarp
High lignin content: 38%
Fuel source
Biochar / Activated Carbon
ME(41%)
EN (31%)
EP (21%)
ED (7%)
Epicarp residue
2.5 – 3.1% protein
45% fibers
7 - 29% lignin
Kernel Oil (Endosperm/Almond)
High oil content: 50-60%
Rich in lauric acid (50%)
Cosmetic and Pharmaceutical industries
Kernel Presscake
22 - 50% protein
34 - 64% fibers
10 - 22% lignin

Biochar production

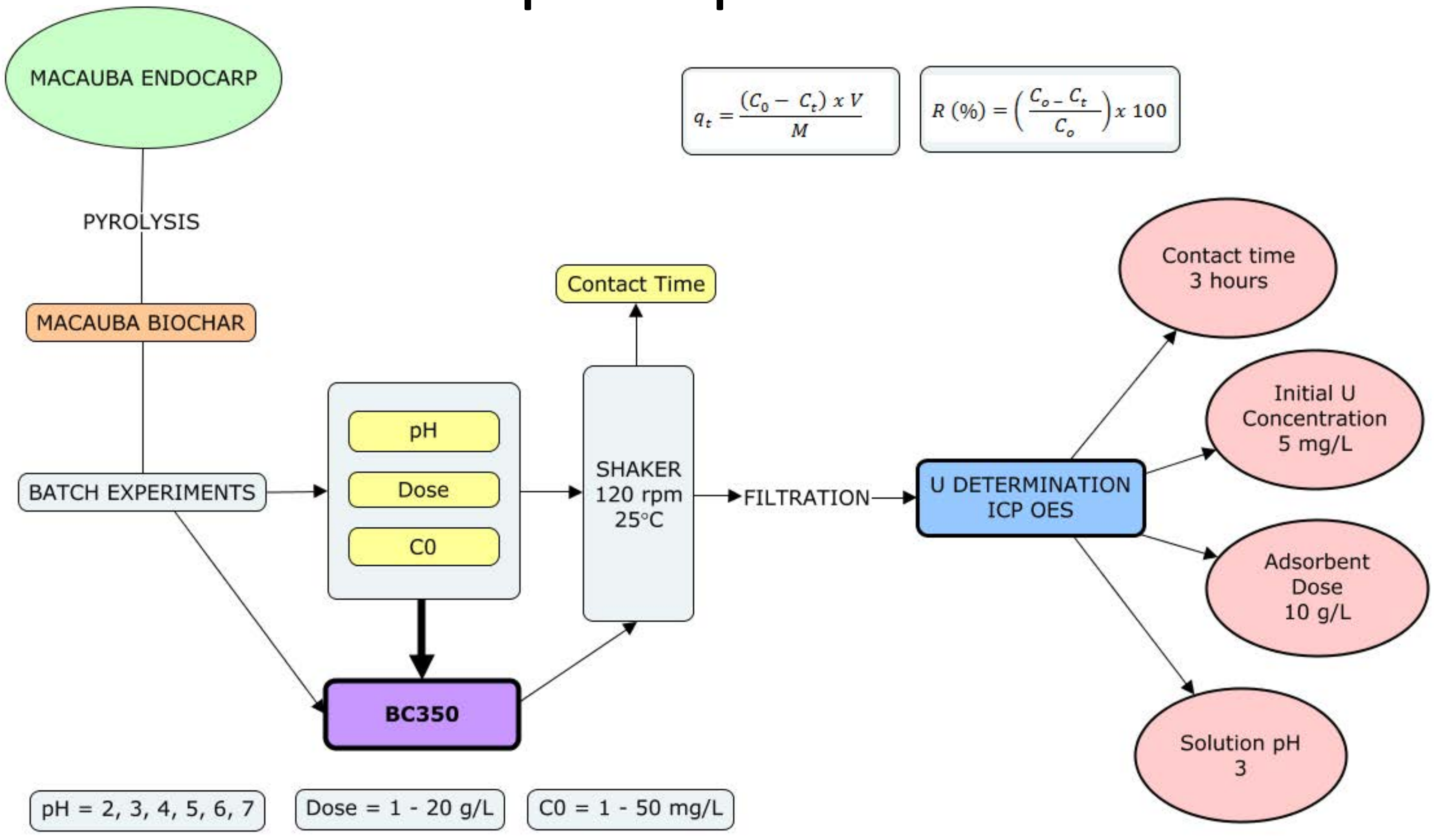


T = 250ºC	BC250
T = 350ºC	BC350
T = 450ºC	BC450
T = 550ºC	BC550
T = 650ºC	BC650
T = 750ºC	BC750

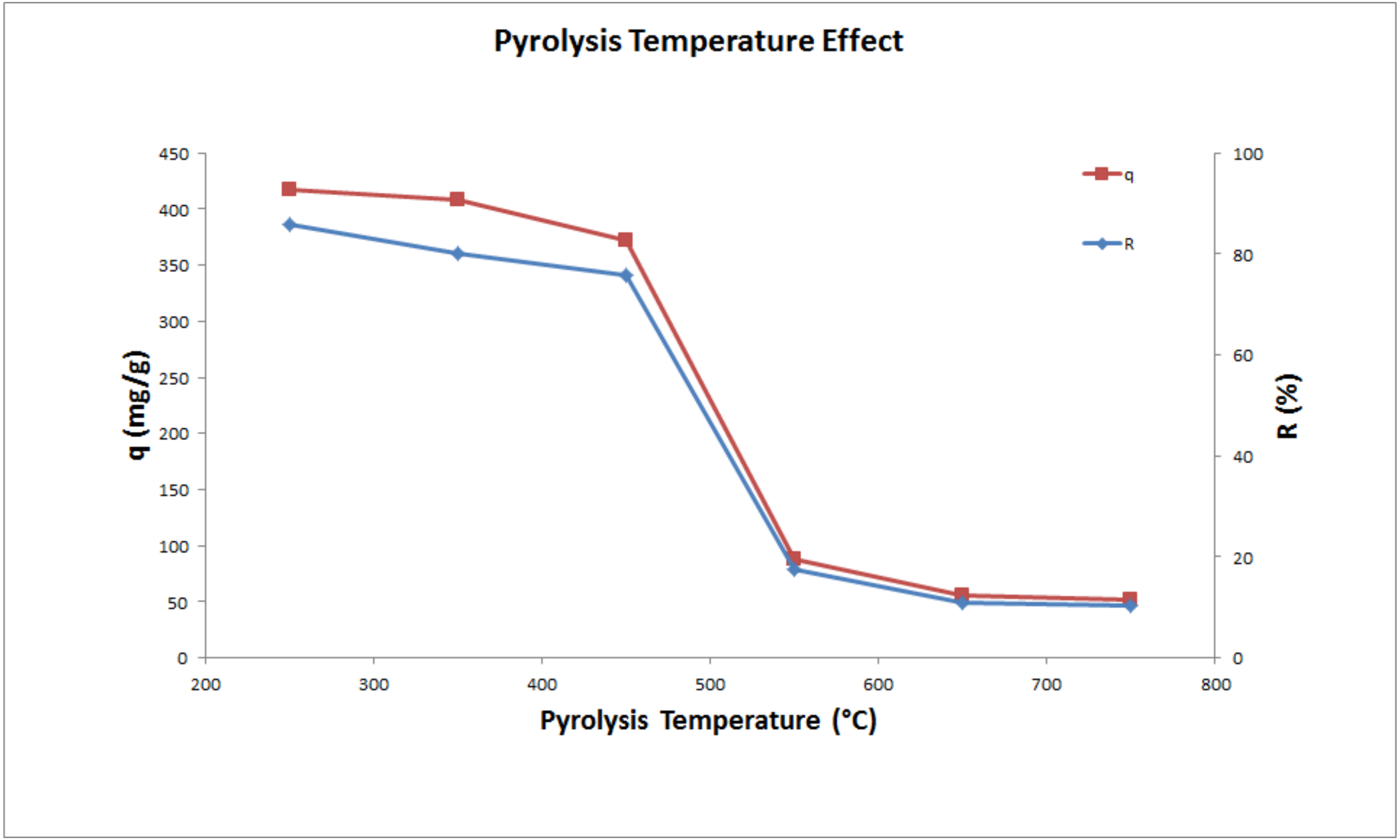
Fixed carbon yield



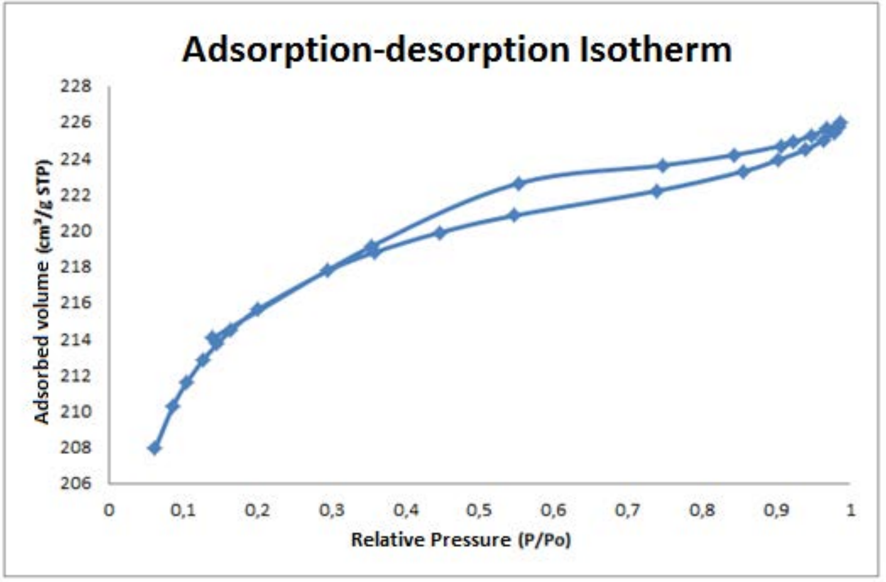
Adsorption parameters



Adsorption experiments



Physical Activation

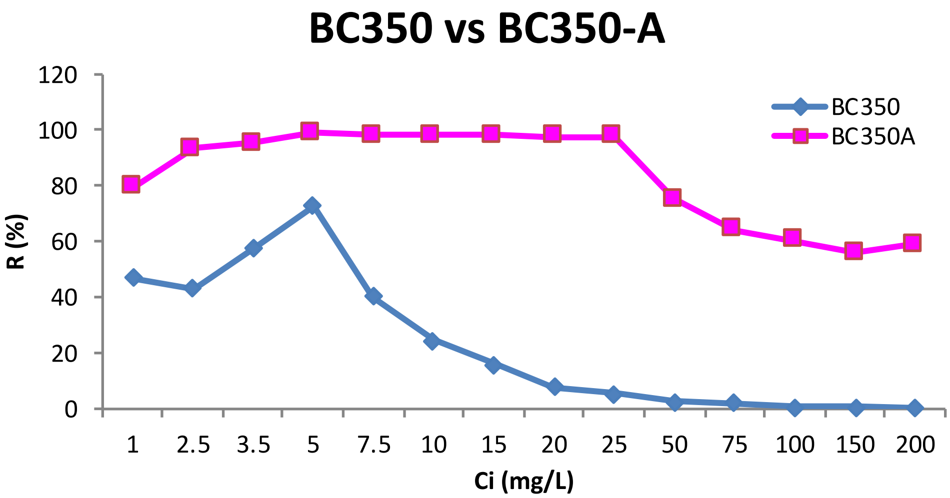


- Physical activation: gaseification process at 850°C using CO_2 atmosphere.
- BC350: non-activated biochar
- BC350-A: activated biochar

Parameters	ASE	V_p	l_{BET}	l_{BET}
BC	(m^2 g^{-1})	(cm^3 g^{-1})	(Å)	(nm)
BC350	0,8320	0,001295	383,181	38,31
BC350-A	643,12	0,298	30,45	3,04

ASE = specific superficial area; V_p = pore volume; l_{BET} = pore size

Results - Activation effect

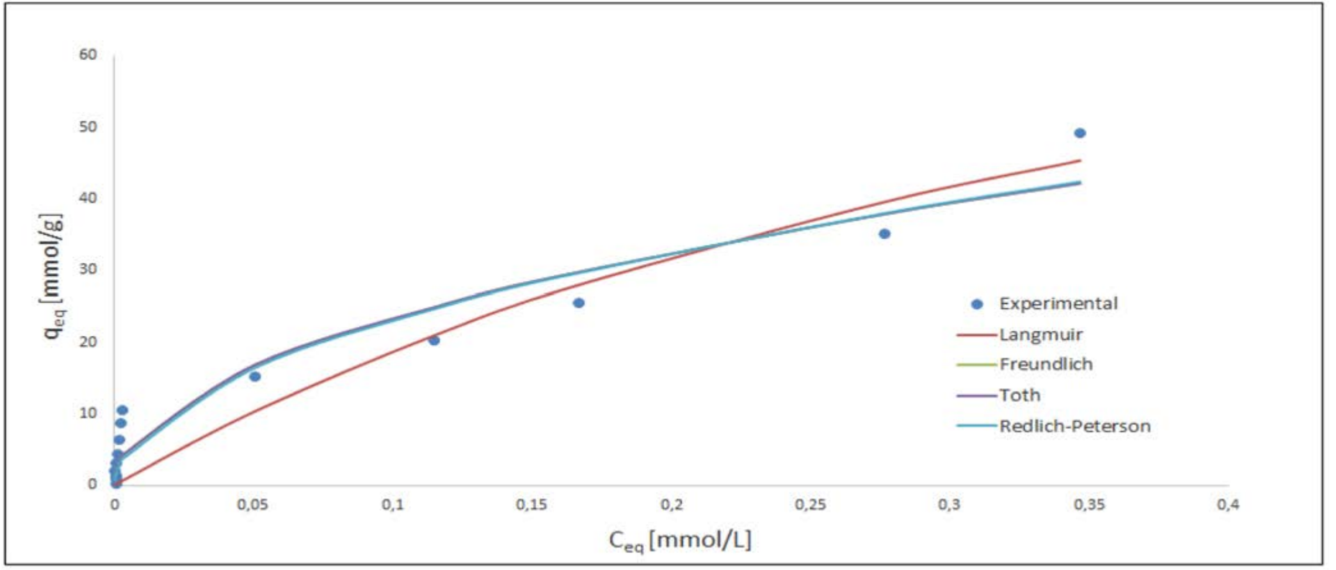


pH = 3; Ci = 1-200 mg/L Dose = 10 g/L; 120 rpm; 25°C

- For a C_i = 5 mg/L, the removal efficiency (R) is above 99% (C_f = 41 mg/L);
- q_{max} = 489 mg/g
- Encompassing concentrations from 2,5 to 25 mg/L.

Adsorbent	q_{max}	References
Chemically and thermally modified bentonite	29	Tsuruta, 2002
Conventional activated carbon	45	Morsy & Hussein, 2011
E. canadensis	89	Yi *et al*, 2016
Thermally treated carbono microspheres	92	Zhang *et al.*, 2013

Results – Adsorption Isotherms



Model	R2	ARE	SSE	MPSD	HYBRID	SAE	X2
Langmuir	0,972	6,10E+01	1,73E+07	2,70E+03	7,27E+04	1,24E+04	1,76E+05
Freundlich	0,968	8,91E+01	**1,08E+07**	2,40E+03	5,78E+04	**1,03E+04**	7,28E+03
Toth	0,968	7,47E+01	**1,08E+07**	2,51E+03	6,32E+04	**1,03E+04**	**7,26E+03**
R-P	**0,974**	**3,99E+01**	1,15E+07	**2,32E+03**	**5,39E+04**	1,04E+04	1,02E+04

Real case application

	Concentration (mg L^{-1})
UF_4 effluent initially generated	76.3
UF_4 effluent after preliminary treatment	5.1
UF_4 effluent after treatment using BC350-A	0.107
Maximum allowable limit (CNEN-NN-8.01)	0.217

- 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.

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ipen

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