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Babassu coconut endocarp-derived activated biochar for efficient cesium adsorption from aqueous solution

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1. Introduction

To reduce greenhouse gas emissions into the atmosphere and make a positive contribution to the environment, biomass is considered as a green alternative because it can be converted into biofuels and bioproducts, such as biochar, through thermochemical processes such as pyrolysis [1]. Recently, studies in the literature have demonstrated the potential of using biochar as an adsorbent in aqueous solutions due to the properties of biochar surfaces such as porous structure, aromatic surface, and the presence of hydroxyl groups [2-4].
Babassu, a plant native to Brazil, has each coconut fruit consisting of an almond, epicarp, mesocarp, and endocarp. It is a biopolymer composed mainly of lignin and cellulose and, due to the inter and intramolecular bonds it can form, it is attractive for use in the adsorption process [5,6]. In the adsorption process, some factors such as pH of the solution, adsorbent dosage, initial concentration of the solution, stirring speed, temperature, and contact time can affect the adsorption and therefore, it is important to optimize them [7].
In addition, biochar can be subjected to physical or chemical activation processes to increase its sorption capacity. However, even though it is an excellent adsorbent, its price is still high for long-term treatment. This fact leads to the use of adsorbents from biological materials, such as activated biochar-derived from babassu coconut [8].
Therefore, in this study, the babassu coconut endocarp-derived activated biochar was employed as an adsorbent for cesium adsorption from aqueous solution. The pH at PZC, pH of the solution, and adsorbent dosage were evaluated to optimize the adsorption conditions for its highest adsorption capacity and for future experiments and characterizations as proposed.

2. Methodology

2.1 Materials and Instrumentation

The activated biochar samples from babassu coconut endocarp were obtained by pyrolysis at 450 ºC and physically activated by CO_2. They were dried in an oven at 100 ºC for 3 h prior to the adsorption experiments. A cesium solution was prepared in ultrapure water and used as standard, at a 280 mg L^{-1}. Ultrapure water with a resistivity of 18.2 MΩ cm^{-1} at 25º C was obtained using a Direct-Q® 3 UV purification system.
A $NaNO_3$ 0.1 mol L^{-1} solution was prepared for PZC study, and a microprocessor-controlled digital pH meter (model DLA-PH, Delfini Industries) was used for pH measurements. The bottles containing the samples from the PZC, and adsorption experiments were shaken at 65 rpm for 24 h on a shaker table NT-145 (New Technique).
For the identification and quantification of cesium-137 activity, a gamma spectrometry system model GX 2518 (Canberra Industries) consisting of a high purity germanium (HPGe) detector was used.

2.2 Point of Zero Charge (PCZ)

To evaluate the pH at PZC of different types of activated biochar, 0.1 g of biochar was added to 50 mL of aqueous $NaNO_3$ solution, under different initial pH conditions. After 24 h of continuous stirring, the samples were filtered, and the final pH was measured. The initial pH was adjusted using HNO_3 0.1 and 1 mol L^{-1} and NaOH 0.5 and 5 mol L^{-1} solutions.

2.3 Adsorption experiments

2.3.1 Effect of adsorbent dosage

For the cesium-137 adsorption studies, the adsorbent dosage was the first parameter evaluated. Cesium concentration was fixed at 280 mg L^{-1} and different adsorbent dosages were tested. After stirring, the samples were filtered to separate the adsorbents.

The adsorption capacity of the adsorbent, q_t (mg g^{-1}), was calculated using the Eq. (1) [7]:

$$q_t = \frac{(C_o - C_t) \; x \; V}{M} \tag{1}$$

where q_t (mg g^{-1}) is the adsorption capacity at any time t, C_o (mg L^{-1}) is the initial concentration of solution and C_t (mg L^{-1}) is the concentration of the adsorbate at time t, V is the volume of the adsorbate solution added (L), and M the amount of the adsorbent used (g).

In addition, the extraction efficiency or percentage removal, R (%), was determined using the Eq. (2) [7]:

$$R(\%) = \left(\frac{C_o - C_t}{C_o}\right) x \; 100 \tag{2}$$

2.3.2 Effect of pH

The second parameter evaluated in Cs-137 adsorption was the effect of pH from aqueous solution. With the solution concentration and adsorbent dosage fixed at 280 mg L^{-1} and 0.40 g L^{-1}, respectively, the pH values were evaluated in a range between 5 and 10.

3. Results and Discussion

3.1 Point of Zero Charge (PZC)

To investigate the superficial charge from babassu coconut endocarp-derived activated biochar in water, the point of zero charge (PCZ) was determined. Has seen, to obtain high efficiency in the adsorption process, the effect of pH is one of the determining factors. Therefore, evaluate the pH of the PZC of BC_{BE} becomes essential. The PZC is defined as the pH where the net surface charge is zero [9]. The results for both types of biochar are presented in Figure 1.

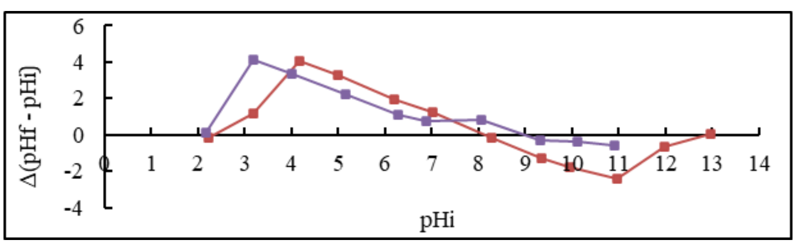

Figure 1: Difference between the final and initial pH as a function of initial pH for granulated (red line) and powdered (purple line) $BC_{BE.}$

As can be seen in Fig. 1, two intersection points corresponding to the PZC of the granulared BC_{BE} are found, at 2.20 and at 8.10. For the BC_{BE} powder, only one intersection point corresponding to its PZC is found, at 9.0.

According to Bandosz & Ania [9], PZC also indicates an increase in the carbon surface acidity or basicity. Thus, the surface of the adsorbent can be considered positively charged when pH < PZC, and the reverse becomes true for pH > PZC.

3.2 Adsorption experiments

3.2.1 Effect of adsorbent dosage

In order to verify the maximum adsorption capacity of the adsorbent in cesium solution, the dosage of BC_{BE} for both types was evaluated in a range between 0.300 to 6.500 g for the granulated BC_{BE} and 0.010 to 0.360

g for the powdered BC_{BE}. The other parameters were held constant (concentration of the cesium solution at 280 mg L^{-1} and volume of solution at 25 mL). The graphs of the adsorption capacity of the adsorbent as a function of the differents BC_{BE} dosages tested are presented in Figures 2 and 3.

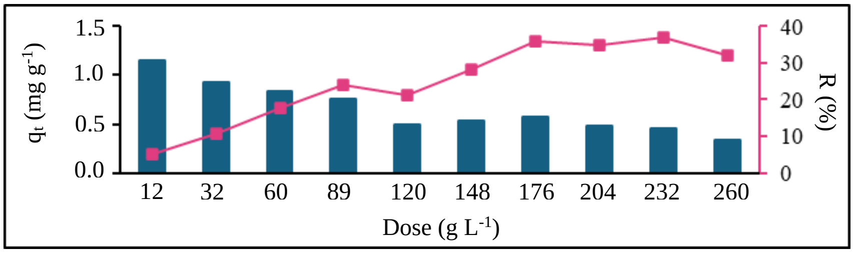

Figure 2: Adsorption capacity (q) of the adsorbent as a function of the granulated BC_{BE} dosage.

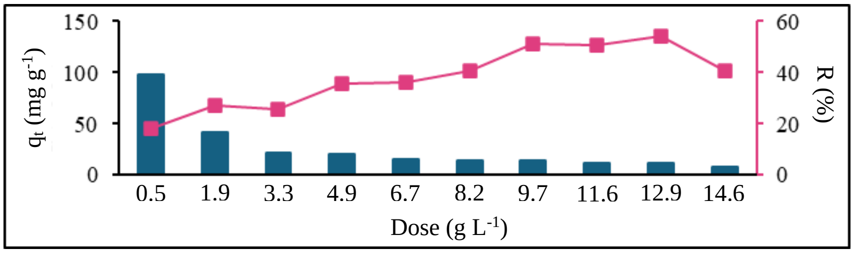

Figure 3: Adsorption capacity (q) of the adsorbent as a function of the powdered BC_{BE} dosage.

As can be seen in Fig. 2 and 3, the adsorption capacity of BC_{BE} and cesium removal percentage show different behaviors. As *q* increases with decreasing dosage, *R* increases with increasing dosage until it begins to hold almost constant. This can be indicative that smaller amounts of adsorbent are necessary for better cesium adsorption.

In addition, the most satisfactory responses for *q* were obtained for the dosages of 12.0 g L^{-1} and 0.40 g L^{-1}, for granulated and powdered BC_{BE}, yielding 1.1475 and 97.634 mg g^{-1}, respectively. Due to the required superior performance, the BC_{BE} in powder was select to evaluate the effect of pH and will be used for future experiments. The adsorbent dosage was fixed at 0.40 g L^{-1}.

3.2.2 Effect of pH

In the adsorption process, pH represents a significant effect on the adsorption capacity of the adsorbent. This can be explained because it affects the surface charge of the adsorbent as well as speciation and the degree of ionization of the metal in solution [10,11]. The pH values were evaluated in a range between 5 and 10 and the results of adsorption capacity of the adsorbent as a function of pH were presented in Figure 5.

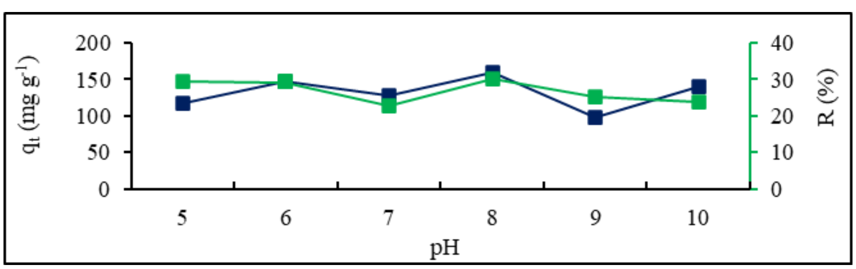

Figure 5: Adsorption capacity (q) of the adsorbent as a function of pH.

As can be seen in Fig. 5, pH 8 represents the optimum pH of the solution with higher adsorption capacity and percentage removal, yielding 161 mg g^{-1} and 30%, respectively. However, as seen, for pH < PZC, the adsorbent surface can be considered positively charged, favoring the adsorption of anions.

Therefore, the result was unexpected and will be further investigated in future experiments.

4. Conclusions

The babassu coconut endocarp-derived activated biochar was employed as an adsorbent of cesium from aqueous solution, being its adsorption capacity evaluated by batch experiments. The pH_{PCZ} for both types of BC_{BE} were investigated, and the initial concentration (280 mg L^{-1}) and volume of the solution (25 mL) were held constant for all adsorption experiments. The results showed that the optimal conditions, that is, the ones that resulted in the highest adsorption capacity for BC_{BE} powder, as well as high percentage removal of cesium were achieved at pH 8, and an adsorbent amount of 0.40 g L^{-1}. The results are satisfactory and demonstrated the potential of the babassu-activated biochar for cesium removal from aqueous solution, with 161 mg g^{-1} of adsorption capacity and 30% percentage removal.
Future experiments will focus on the experimental design for parameter optimization, followed by kinetic and isothermal studies. Desorption and regeneration will also be conducted to evaluate the potential reusability of the biochar. Additionally, to further elucidate the effectiveness of BC_{BE}, a comprehensive characterization, before and after adsorption, by FTIR, and, SEM, its application in real radioactive waste with optimized parameters will be performed.

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