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Adsorptive removal of Rhodamine B using kapok pods hydrocarbon

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Abstract

The contamination of water resources has led to research aimed at minimizing environmental impacts. The use of charcoal as an adsorbent is a sustainable and highly efficient alternative for removing persistent pollutants such as Rhodamine B (RhB). The aim of this study was to evaluate the adsorptive potential of kapok pod hydrocarbon against RhB. To this end, tests were carried out on adsorbent mass, pollutant concentration, pH and adsorption in a continuous flow. In the affinity and pH tests, a strong interaction between adsorbent and adsorbate was observed. The material presented a high adsorptive capacity (107 - 373 $mg.g^{-1}$). Its performance was efficient at low and high concentrations, with around 87% removal of RhB - 5 ppm. In the continuous flow tests, total removal of the pollutant was achieved in a 2.5 ppm RhB solution, making it a sustainable and low-cost alternative for removing dyes from aqueous effluents.

Keywords: Waste reuse; value-added products; water purification; environmental remediation; continuos flow process.

1. Introduction

The scarcity of drinking water and the pollution of water resources have been major socio-environmental challenges. One of the problems related to water quality is the various types of solid and liquid waste disposed of inappropriately in receiving bodies, which has had devastating consequences for the environment [1]. Against this backdrop, various studies have been carried out with the aim of improving processes and minimizing environmental impacts.

Agricultural production is responsible for a large proportion of waste generation. Brazil is one of the world's leading agricultural producers, and consequently generates a large volume of waste. One of the alternatives to disposing of this waste is the manufacture of biocarbon, due to its versatility of application, from use in the purification of water and effluents, as a high-performance adsorbent or even its application as a biofertilizer and soil conditioner [2, 3]. The use of biomass in adsorption processes has gained prominence due to the relevance of adsorption as a highly efficient technique for removing pollutants harmful to the environment [4, 5].

Various types of waste can be used to produce charcoal, including kapok pod husks, since in their natural state they already have interesting physical and chemical properties due to their high surface area, presence of vacancies, roughness and presence of functional groups that presented high adsorptive potential when applied to liquid effluents [6].

The group of hazardous contaminants includes those considered to be persistent, among them Rhodamine B (RhB), which is a cationic dye from the xanthenes class, widely used in industry. It is a pigment that is laborious to remove and poses a risk to human health, as it is mutagenic, carcinogenic, neurotoxic and bioaccumulative [7].

In view of the problems raised, the aim of this study was to evaluate the potential of kapok pod hydrocarbon for removing RhB from aqueous solutions in a fixed-bed system.

2. Methodology

2.1 Materials

The fruits of the Paineira were collected directly from the kapok tree, located at the Federal University of Alagoas in the municipality of Maceió - Al, between the months of fruit ripeness. The fiber,

pod skin and seeds were separated. The husks were crushed and sorted through 32 mesh sieves.

2.2. Experimental

2.2.1 Hydrochar production

The hydrocarbon was produced using the adapted hydrothermal method [8], using 5g of material in 50 mL of distilled water and stirred for 30 min, then transferred to an autoclave reactor in a PTFE container and kept in an oven for 6 hours at 160 ºC. The hydrocarbon was then washed with distilled water until a clear residual liquid came out and then transferred to a muffle furnace and kept at 200 ºC for 2 hours.

2.2.2 Affinity test

The affinity test was conducted in different pH ranges in order to verify the interaction between the adsorbent and the adsorbate and in which pH regions this interaction may or may not be favored. The study was carried out at pH 3; 4.8 (natural pH of the solution), 7 and 12 with 16 hours of contact, under agitation of 200 rpm in a Shaker at 25 °C. The system was set up using 0.01 g of adsorbent and 50 mL of solution at a concentration of 10 ppm. Sulphuric acid and sodium hydroxide, both at 0.1mol. L^{-1}. Finally, the final concentration of RhB was determined using an Ultraviolet-Visible Spectrophotometer, Shimadzu, model UV-1800, using a calibration curve at a wavelength of 557 nm. The mass variation test was carried out using 0.01, 0.05 and 0.25 g of adsorbent in 50 mL of RhB solution at 50ppm. For concentration variation, 50 mL solutions of 5, 10, 50 and 100ppm at natural pH and 0.05g of adsorbent were used.

2.2.3 Fixed bed test

The fixed bed test was carried out in a glass column with an internal diameter of 1.5 cm and a height of 15 cm. The kinetic effluent was introduced in an upward flow using a peristaltic pump, the bed outlet was positioned at the top of the column and the RhB concentrations analyzed were 2.5 and 50 ppm. For the bed mass, 0.5 g of adsorbent was used, interspersed with 4 mm glass microbeads forming a 5 cm bed. The breakthrough curves were built at a flow rate of 1 mL/min and 500 mL of volume to be treated. To construct the breakthrough curves, C/C_o versus time was considered and samples were taken at the column outlet at different time intervals. The kinetic data was adjusted using the mathematical model of Thomas Eq (1)

$$\ln\left(\frac{Co}{Ct} - 1\right) = \frac{k_{Th}\, q_m M}{Q} - k_{Th}\, C_O t \qquad (1)$$

Where C_o is the initial concentration, C_t is the concentration at a given time, both in ($mg.L^{-1}$), k_{Th} is Thomas' constant, q_m is the maximum adsorption capacity ($mg.g^{-1}$), M is the mass of the adsorbent in (g), Q is the flow rate ($mL.min^{-1}$) and t is defined by Eq (2).

$$t = \left(\frac{V_e}{Q}\right) \qquad (2)$$

Where V_e is the effluent volume in the column.

3. Results and discussions

3.1 Affinity

The affinity test showed that the adsorbent and adsorbate had a high affinity, as can be seen in fig. 1(a). In the four pH ranges applied, the material had a strong interaction, showing pollutant removal of more than 25% at natural pH and in pH 12, at pH 3 its performance was greater than 19% removal, while at pH 7 it did not exceed 10.5%. In view of this, natural pH was chosen for the other tests. In the mass variation tests, it was observed that the mass of 0.01g provided a removal of only 12.8%, the mass of 0.05g provided a removal of more than 4.8% and with 0.25g the removal was 91.9%, as shown in fig. 1(b). However, it is clear that increasing the mass led to a significant increase in the percentage removal of the pollutant; as the mass was increased from 0.01 to 0.05g, an increase in removal of approximately 12% was observed, while when the mass was increased from 0.05 to 0.25g, the increase in the percentage of removal was around 67%, although there was a considerable increase, the 5x increase in mass was not enough to increase the percentage of removal in the same proportion, causing a reduction in adsorptive capacity, due to not filling the available active sites and consequently increasing the costs of treating the effluent. It was therefore decided to work with a mass of 0.05g, since this had a wide removal

potential and high adsorption capacity, minimizing material costs.

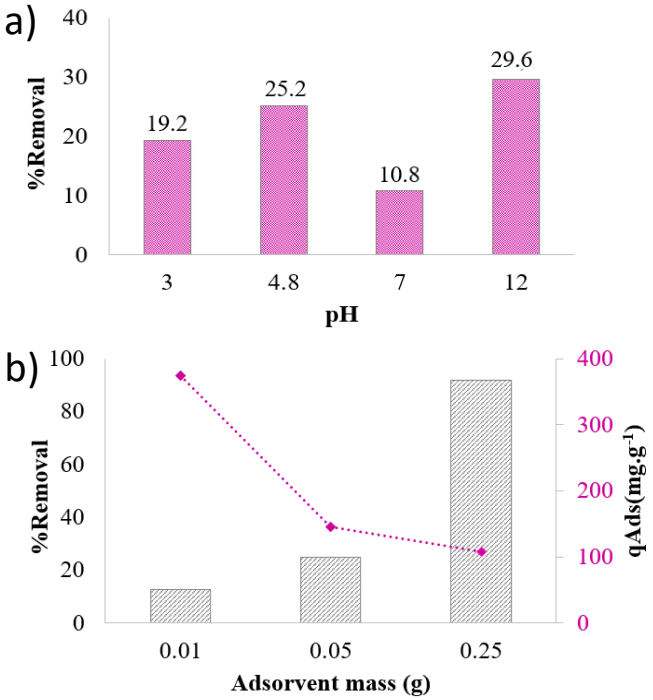

Fig. 1. (a) Affinity and pH tests. (b) Adsorbent mass test.

The concentration test showed that the material performed excellently at the four concentrations applied as can be seen in Fig. 2.

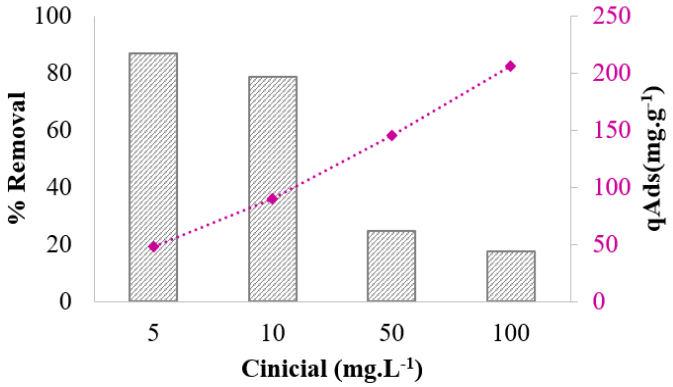

Fig. 2. RhB concentration variation test.

At the concentrations studied, its removal was 87; 78.8; 24.8 and 17.6% at 5, 10, 50 and 100 mg.L^{-1} of RhB respectively, with adsorption capacity ranging from 48 to 205 mg.g^{-1} in the tests applied. The tests carried out showed that the material performed well at low and high concentrations of the pollutant, which, when applied to a real case, could mean that the adsorbent was used satisfactorily, even in situations involving trace concentrations.

3.2 Fixed bed test

In the first tests, the breakthrough curve constructed for the initial concentration of 2.5 mg.L^{-1} of RhB, as shown in fig. 3(a). The calculated q_m was 5.75 mg.g^{-1}, compared to the Thomas adjustment model, the q_m was 53.43 mg.g^{-1} and k_{Th} 0.094 mL.mg $^{-1}$.min^{-1} with a superior R^2 adjustment of 0.9. It was observed that the theoretical value was much higher than the experimental one, which can be explained by the fact that the bed had not reached saturation and had removed all the pollutant contained in the 500 mL treated. He low kTh value suggests slow adsorption, which may have caused a discrepancy between the simulated and experimental qm.

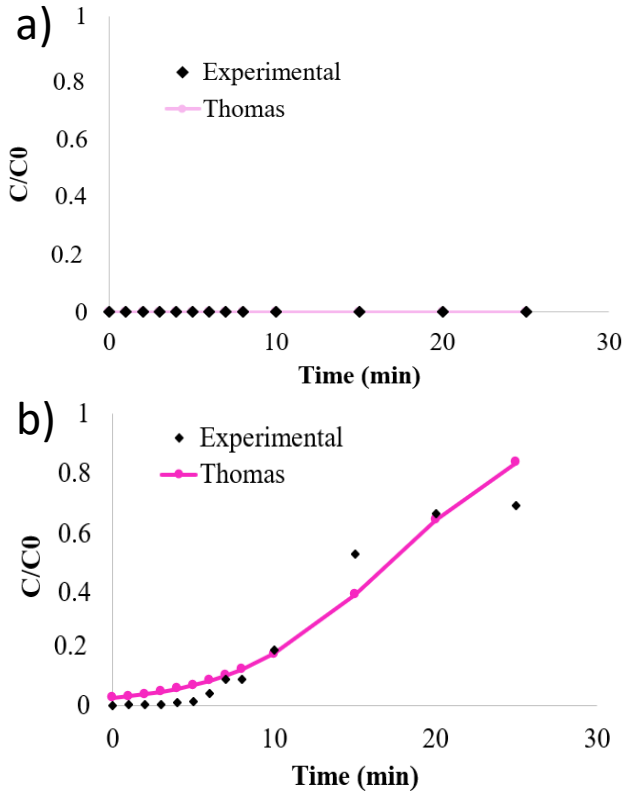

Fig.3. (a)Fixed bed adsorption breakthrough curve for RhB at 2.5 ppm and (b) 50 ppm.

In test two, Figure 3(b), the initial concentration was 50 mg.L^{-1}, the breakthrough concentration was

calculated at 5.78 mg.L-1 and the experimental qm was 0.29 mg.g- 1, compared to the adjusted qm, which was 2 mg.g-1 and kTh 0.003 mL.mg-1.min-1, with R2 greater than 0.94. This test also showed that the theoretical qm was 10 times greater than the experimental qm and consequently low kTh, suggesting slow adsorption and possible non-filling of available active sites, in a similar way to test 1. This situation was observed by [6], when used the fresh kapok capsule in a fixed bed to remove RhB, varying concentrations from 2.5 to 100 ppm. Although the material presented an experimental adsorption capacity lower than the adjusted one, the overall pollutant removal was greater than 74%, showing excellent adsorbent performance in both cases studied.

Observing the batch and continuous tests, it was possible to verify that the increase in mass resulted in a reduction in the adsorptive capacity, this fact may be associated with the non-filling of active sites caused by the agglomeration of the adsorbent, making the diffusion process difficult.

4. Conclusions

The main objective of this work was to assess the feasibility of producing a hydrocarbon from the husk of the kapok pod as a low-cost adsorbent. From the analysis of the material's performance, it is possible to infer that under the conditions applied, the material proved to be an excellent adsorbent. In the affinity and pH variation tests, a strong interaction between adsorbent and adsorbate was observed in all the ranges applied. In the mass variation test, the material had a very high adsorption capacity, ranging from 107 to 373 $mg.g^{-1}$, removing between 91 and 13 % of the pollutant, respectively. In the concentration variation test, the hydrocarbon showed excellent performance, with 87 % removal at 5 $mg.L^{-1}$ of RhB in solution. In the fixed-bed tests, the adsorbent proved to be a highly industrially applicable material, since it performed well at low and high pollutant concentrations under the conditions employed. Furthermore, in the worst-case scenario, its performance was high, guaranteeing total removal of over 74 % in relation to the total volume treated, and it could also be applied under trace concentration conditions.

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