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STUDY OF THE ADSORPTION POTENTIAL OF NATURAL PEQUI SHELL AND ENDOCARP (*Caryocar Brasiliense*) FOR METHYLENE BLUE

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ABSTRACT

This study aimed to evaluate the adsorptive potential of the natural peel and endocarp of pequi (*Caryocar brasiliense*) for methylene blue adsorption in aqueous solutions, with the goal of promoting the adsorption method using bioadsorbents for treating contaminated aqueous effluents. Pequi is a fruit native to the Brazilian Cerrado and is widely found in the Central-West region. Its almond is sold in local markets, but much of the fruit is wasted due to the spines present around the endocarp, which make it difficult to consume. Thus, pequi was chosen due to its high availability, with the objective of reducing its waste by using it as a bioadsorbent. The experimental methodology included drying at 100 °C for 24 hours grinding the peel and endocarp with a knife mill. Particle size was determined using 42-mesh sieves, and sample analysis was conducted with a spectrophotometer at a wavelength of 660 nm. Experiments were performed in triplicate and in batch mode at different temperatures (25, 35, and 45 °C) and contact times (5, 10, 15, 20, 25, 30, and 40 minutes). Results showed that at 25 °C, the peel achieved a maximum removal of 84.70% (± 1.41) and the endocarp 78.02% (± 6.08) in 40 minutes. At 35 °C, the peel achieved a maximum removal of 89.95% (± 0.80) and the endocarp 83.62% (± 3.96). At 45 °C, the maximum removal was 87.97% (± 0.87) and 85.16% (± 5.10) for the peel and endocarp, respectively. It is worth noting that at 25 °C, equilibrium time was not observed for either adsorbent, indicating that adsorption sites were not saturated, requiring more time than the studied interval. Based on the results obtained, it can be concluded that adsorption using the natural peel and endocarp of pequi is an effective and promising method for treating aqueous effluents due to the low cost, high removal efficiency, and high availability of the bioadsorbent.

Keywords: Bioadsorbent. Biomass. Kinetics. Dyes. Textile Effluent.

1. INTRODUCTION

The first industrial revolution, which occurred in the mid-18th century, introduced significant advancements for humanity, such as the power loom. However, to keep up with society's demands, the industry was compelled to produce on an ever-larger scale (Sakurai and Zuchi, 2018). Consequently, the amount of aqueous effluents produced increased significantly. Among the industries that generate such waste, the textile industry stands out, as dyeing a single t-shirt consumes between 16 and 20 liters of water (Lee, 2009). Therefore, treating the aqueous effluents produced by it becomes necessary.

There are three main methods for treating aqueous effluents: chemical, biological, and physicochemical. Chemical methods involve

processes where removal occurs through chemical reactions, such as oxidation, ozonation, or electrochemical destruction. However, they generally present high costs and environmental challenges related to the disposal of reagents and by-products (Wang et al., 2018). Biological methods are sustainable and economical, but they are highly sensitive to environmental changes, making large-scale implementation difficult (Silveira, 2013). Among physicochemical methods, adsorption stands out due to its low complexity and high removal capacity (Kwon and Lee, 2015).

In this context, adsorption is a physicochemical method involving the presence of

an adsorbent, an adsorbate, and a solvent (Ruthven, 1984). Among various adsorbents, bioadsorbents are notable because, in addition to contributing to sustainability, they are readily available in nature.

Pequi can be divided into: epicarp (peel), external and internal mesocarp (pulp), endocarp, which has small, fine spines around it, making it difficult to consume, and an edible almond that is commercially used in local agriculture. The epicarp and external mesocarp are usually treated as by-products, often being discarded (Siqueira et al., 2013). The pulp has high antioxidant potential due to its composition, and the almond is widely used for oil extraction. According to Melo et al. (2021), 45 individuals/ha can produce about 180 kg of pulp, 119 kg of pulp oil, 33 kg of almonds, and 15 L of almond oil. Therefore, adsorption using the endocarp of pequi (*Caryocar brasiliense*), a fruit abundantly found in the Brazilian Cerrado and classified as a bioadsorbent, shows potential for treating aqueous effluents due to its high efficiency, operational simplicity, and low cost.

Thus, this study aims to investigate the potential of the natural shell and endocarp of pequi in the adsorption of methylene blue dye in aqueous solution at different temperatures and contact times.

2. MATERIALS AND METHODS

2.1. Adsorbent Preparation

Initially, the pequi parts were separated, selecting the peel and endocarp. They were washed with running water and left to air-dry for three days (at room temperature). Then, the samples were placed in an oven at 50 °C for 24 hours. Afterward, the bioadsorbent were ground separately in a knife mill (Tecnal, Te048) and left again in the oven under the same previous conditions. Finally, the samples were passed through a vibrating table (Bertel) with sieves of different meshes to separate the different particle sizes. The particle size chosen for this study was 42 mesh.

2.2. Batch Adsorption Potential Evaluation of the Adsorbent

All experiments presented in this study

were performed in triplicate to assess the influence of contact time and temperature on the adsorption of natural peel and endocarp. Thus, experiments were conducted in 125 mL Erlenmeyer flasks containing 25 mL of methylene blue aqueous solution (100 mg/L adsorbate) and 0.05 g of adsorbent. The sample was subjected to different temperatures (25, 35, and 45 °C) and contact times (5, 10, 15, 20, 25, 30, and 40 minutes) under constant agitation in a shaker (Pro lab, Sk-O180-Pro digital) at 360 rpm connected to a thermostatic bath (Tecnal, TE2005) to maintain the temperature. After the desired time, the solution was filtered to stop contact between the adsorbent and adsorbate.

The filtered solution was analyzed in a UV-visible spectrophotometer (Bel UV-M51) at a wavelength of 660 nm. Based on the calibration curve constructed for the methylene blue solution, absorbance was converted to the final concentration (mg/L). To calculate the amount of material adsorbed at a given time (Q_t) in mg adsorbed/g of adsorbent, equation 1 was used.

$$Q_t = (C_i - C_f) * \frac{m}{V} \quad (\text{Eq. 1})$$

where C_i and C_f (mg/L) are the initial and final concentrations, respectively, V is the volume (L) of the solution, and m is the mass (g) of the adsorbent.

3. RESULTS AND DISCUSSION:

3.1. Effect of Contact Time

The study of contact time is essential to determine the equilibrium time of an adsorption process, as it enables the assessment of the maximum adsorbed quantity under the tested conditions (Yu et al., 2013). The time range studied was between 0 and 40 min for experiments conducted using the endocarp and peel at 25°C. Within the selected range, it was not possible to establish the equilibrium time for either bioadsorbent, as the adsorbed quantity did not reach equilibrium; that is, the available adsorption sites were not fully occupied, requiring a longer adsorption time.

Figure 1 represents the kinetic curves of the amount adsorbed by the endocarp and peel at 25 °C. Since the experiments were performed in triplicate, the results presented represent the

average of these trials.

It is noteworthy that between 5 and 40 min, the adsorbed quantity increased significantly over the interval. The process proved more effective over a longer duration; thus, 40 min would be the optimal time for treating the methylene blue solution using the peel and endocarp, providing speed and efficiency.

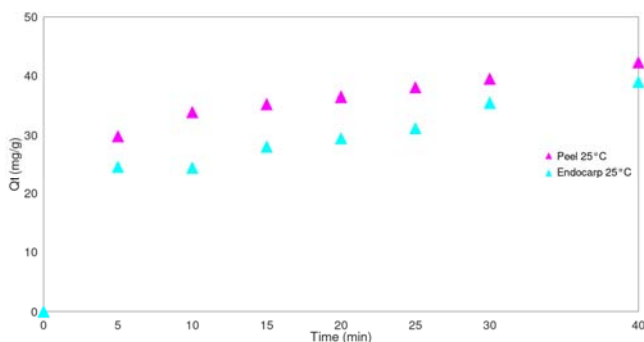


Figure 1. Kinetic curves showing the adsorbed quantity as a function of contact time for adsorption using the natural endocarp and peel of pequi at 25 °C.

Additionally, it can be observed that the peel exhibited a higher adsorbed quantity compared to the endocarp; this is due to the peel having a larger and more porous surface area, as well as more functional groups that facilitate adsorption (Amorim et al., 2016).

In Figure 2, the efficiency of the adsorption process using the natural endocarp at 25 °C can be seen through the change in color of the aliquots, indicating that the dye concentration decreased over time.



Figure 2. Illustration of the solutions after 0, 5, 15, and 30 min at 25 °C.

3.1. Effect of Temperature

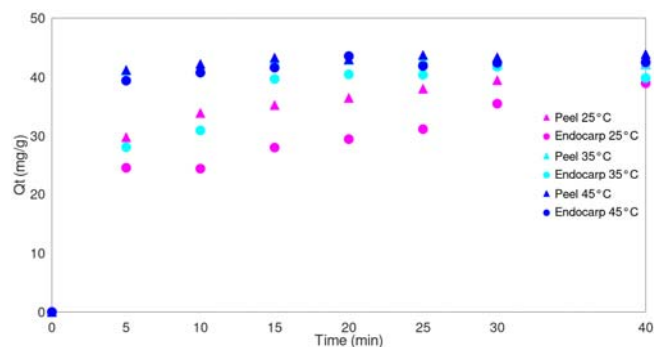


Figure 3. Effect of temperature on adsorbed quantity as a function of time using the natural endocarp and peel of pequi at 25, 35 and 45 °C.

Figure 3 presents the average kinetic adsorption curve using the endocarp and the peel at times of 5, 10, 15, 20, 25, 30, and 40 minutes and at temperatures of 25, 35, and 45 °C. From this figure, it is possible to observe that at 25 °C, the endocarp presented a Q_t of 38.93 (± 2.99) mg/g, while the peel presented 42.27 (± 0.65) mg/g. On the other hand, at a temperature of 35 °C, the maximum amount removed by the peel was 44.03 (± 0.66) mg/g, while the endocarp reached 41.76 (± 1.97) mg/g. Finally, the temperature of 45 °C proved to be the most effective for the adsorption process, as the peel achieved a maximum Q_t of 43.90 (± 0.87) mg/g and the endocarp, 42.50 (± 2.48) mg/g.

After analyzing the results across all temperatures, it was found that the adsorption process proved more efficient at higher temperatures, achieving equilibrium faster. Additionally, the maximum adsorbed quantity varied little between 35 °C and 45 °C, demonstrating that temperature changes affect the speed of the adsorption process but not the maximum adsorbed quantity.

The equilibrium time is reached when the removal after that point does not vary significantly, meaning all sites have been occupied. Thus, within the studied range, no equilibrium time was observed at a temperature of 25 °C, requiring a longer time. At 35 °C, the equilibrium time was reached in 15 minutes for the peel and 20 minutes for the endocarp. At 45 °C, the sites became saturated more quickly, being 10 minutes for the peel and 15 minutes for the endocarp.

Thus, the high efficacy of the process using natural bioadsorbents is evident, reducing costs for implementing the process at an industrial level, as no thermal treatment is required to achieve satisfactory results.

For future research, it is recommended to

test the adsorption process with thermal treatment and at different pH ranges. Additionally, it is worthwhile to study adsorption in continuous operation mode using an adsorption column.

4. CONCLUSIONS:

The adsorption method using the natural peel and endocarp of pequi for the removal of methylene blue dye in an aqueous solution proved technically viable. Among the three temperatures studied, 45 °C was the most effective, adsorbing the largest amount (87,97 % for peel and 85,16% for endocarp). Therefore, it can be concluded that the process at 25 °C is not spontaneous. In this context, the use of biomass as an adsorbent is considered viable, as it is cost-effective and abundant compared to other synthetic materials.

5. DECLARATIONS

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