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Effect of demineralization and heat treatment of shrimp shells in a non-inert environment on the production of biosorbents

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Abstract

Shrimp processing generates waste that accounts for approximately 40 to 50% of the crustacean's weight and, as it is an expanding crop, it is essential to invest in the entire production chain to avoid improper disposal and environmental impact. In this context, this study investigates the effect of demineralization and heat treatment in a non-inert environment to produce adsorbents capable of removing pollutants. The shrimp residue was dried and ground, with part of it demineralized in 1 M HCL for 6 hours and washed until neutral before drying. After grinding, a portion was subjected to carbonization in a muffle furnace at 600 °C for 1 hour, followed by washing to remove ash. The surface characterization of the adsorbents was carried out using FTIR, Boehm titration and determination of the zero charge point. During demineralization, partial removal of $CaCO_3$ was observed and the heat treatment significantly contributed to the development of an improved structure compared to the natural residue. Batch adsorption tests showed that demineralization and calcination could remove 100% of methylene blue (50 mg L^{-1}) in just 10 minutes of contact.

Keywords: Shrimp farming; adsorption; methylene blue; reuse.

1. Introduction

According to data from the IBGE (Brazilian Institute of Geography and Statistics), Brazilian shrimp farming reached approximately 113,300 tons of shrimp in 2022, valued at R$ 2.23 billion, a value 59.3% higher than in 2020, with the largest producers concentrated in the Northeast region of the country [1].

As shrimp farming is an expanding industry, investing in the entire production chain is necessary. The residues, made up of the head, carapace and tail, resulting from the shrimp processing process, represents 40 to 50% of its total weight. These residues are classified as class II due to their rapid deterioration, leading to significant environmental issues [2]. However, they can be used to acquire greater added value, as they mainly consist of pigments (1-14%), chitin and carotenoids (15-30%), proteins (25-40%) and calcium carbonate (30-55%) [3,4].

Despite the widespread use of chitin and chitosan extracted from shrimp shells in the treatment of effluents, Rojas *et al*. [5] mentioned that the residue can also be used as a biosorbent. This is an attractive alternative for removing dyes, heavy metals, and other pollutants due to its low cost, easy implementation, versatility and rapid kinetics.

Different thermochemical conversion technologies, which vary depending on operating conditions such as the atmosphere used (e.g. air, O_2, N_2), residence time, heating rate and temperature, can generate biochar [6]. This process often results in a significant increase in the specific surface area and the formation of a well-defined porous structure, altering the surface and chemical functionality of the residue. This results in a material with improved adsorption capacity [7].

In shrimp waste, studies also highlight the importance of removing part of the $CaCO_3$ present in the shell to increase specific surface area and reduce ash content [8]. This favors physical activation, due to the interaction of the biomass with the CO_2 released during the decomposition of $CaCO_3$, which occurs at temperatures between 570 and 800 °C, significantly contributing to the development of micropores in the material [9].

This study seeks to explore how demineralization and heat treatment of shrimp shells in a non-inert

environment can produce adsorbents for effectively removing methylene blue (MB) dye.

2. Materials and Methods

2.1. Preparation of the adsorbent

Shrimp shells were obtained from local market. The raw material was initially cleaned in running water to remove residues of organic matter adhered to the shells. Then, one part was sanitized using 150 ppm sodium hypochlorite for 15 min, while the other underwent demineralization pretreatment.

For the demineralization process, the shells were immersed in a 1 M HCl solution, in a ratio of 1:5, for 6 h at room temperature, with occasional stirring. The material was then washed until it reached a pH close to neutrality.

Both parts, after the respective treatments, were dried in an oven at 50 °C until they reached a constant weight and then ground in a ball mill (Retsch, PM100). The raw samples were designated according to the demineralization treatment. The sanitized sample was named untreated (ST) for comparison purposes.

To produce biochar, the demineralized sample was placed in crucibles and heated in a GP Científica muffle furnace at 600 °C for 1 h. After cooling, the material was repeatedly washed with distilled water at a temperature between 70 and 80 °C and, followed by room temperature, until reaching neutrality to remove ash during the process. Subsequently, the material was dried in an oven at 100 °C and sieved through a 200 mesh sieve to ensure particle uniformity, resulting in the final biochar, designated as CT carb.

2.2. Characterization of the adsorbent

Surface functional groups analyses of the adsorbents was carried out using FTIR (Fourier-Transform Infrared Spectroscopy) with a Shimadzu spectrometer model IRPrestige-21, and by titration, according to Boehm's methodology [10].

The determination of pH at the point of zero charge (pHpzc) was carried out using the 11-point method, as described by Regalbuto *et al*. [11].

2.3. Adsorption assays

Batch adsorption experiments were conducted to evaluate the adsorption of MB. 50 mg of adsorbents were placed in contact with 5 mL of MB solution at 50 mg L^{-1}, at times of 0, 5, 10, 15, 30 and 60 min.

Absorbance readings were taken using an LGI Scientific UV-VIS spectrophotometer, model LGI-VS-721N, at a wavelength of 660 nm. The adsorption capacity (q, mg g^{-1}) and the removal percentage were calculated according to Equations 1 and 2, respectively.

$$q = \frac{(C_0 - C_f) \times V}{m} \quad (1)$$

$$\% \text{ removal} = \frac{(C_0 - C_f)}{C_0} \times 100 \quad (2)$$

where, C_0 is the initial concentration of the adsorbate solution (mg L^{-1} or g L^{-1}), C_f is the final concentration of the adsorbate solution (mg L^{-1} or g L^{-1}), V is the volume of the adsorbate solution (in L) and m is the mass of the adsorbent used (in g).

3. Results and Discussion

3.1. Characterization of the adsorbent

FTIR spectra (Fig. 1) showed peaks at 1487 cm^{-1} attributed to the antisymmetric stretching vibration of CO_3^{-2}, indicating the presence of $CaCO_3$ in the form of calcite [12]. Additionally, the OH stretching vibration region was observed between 3300-3500 cm^{-1}, suggesting the presence of alcohol and phenol structures in biochar after the thermal process, which is a characteristic of functional groups in biochars [9]. Peaks at 1348 and 1618 cm^{-1} were identified and attributed, respectively, to the carboxyl [13] and amide I (C=O) [9] groups.

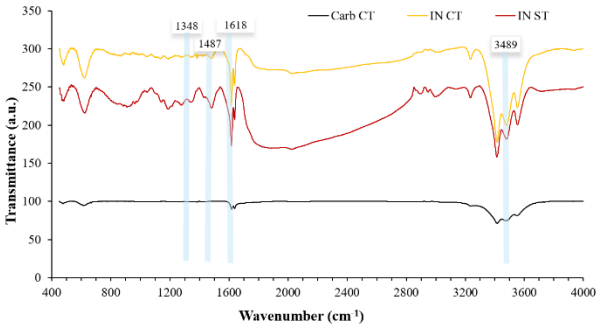

Fig. 1. FTIR spectra of the adsorbents.

Table 1 shows the values obtained in the Boehm test, which are consistent with the observations from the FTIR analysis. It is noteworthy that the carboxylic acid peak decreases from the IN ST sample to the IN CT and is not present in the Carb CT, aligning with the negative value obtained in the test. The presence of the OH band indicates the presence of the phenolic group.

Table 1. Boehm titration values

Sample	Basic (mEq g^{-1})	Acid (mEq g^{-1})		
		Carboxylic	Lactonic	Phenolic
IN ST	3.21	0.20	-0.49	0.29
IN CT	0.05	0.34	-0.83	0.49
Carb CT	0.65	-0.45	0.15	0.30

Furthermore, the peak related to calcium carbonate decreases in the IN CT sample compared to the IN ST sample, indicating that demineralization did not completely remove the calcium carbonate. The absence of this peak in the Carb CT may suggest that there was complete decomposition of $CaCO_3$ into CaO, according to Equation 3, since it is not visible in the spectrum.

$$CaCO_3 \rightarrow CaO + CO_2 \quad (3)$$

3.2. Adsorption assays

Batch adsorption tests were carried out using biosorbents derived from shrimp shells to evaluate their capacity as an alternative and low-cost adsorbent. In Fig. 2, the percentage of removal of the 50 mg L^{-1} MB solution at different contact times is shown. The adsorbent derived from demineralized shrimp shell (IN CT) showed a low removal efficiency compared to the natura adsorbent (IN ST) and its biochar. In comparison, CT carb achieved 100% solution removal within 10 minutes of contact, while IN ST achieved 83%, highlighting the importance of heat treatment in improving adsorbent properties such as stability and surface area.

Fig. 3 shows the adsorption capacity profiles (q) over contact time. Kinetic equilibrium is quickly reached for all samples tested, with significant dye adsorption within the first 30 seconds. This indicates the efficiency of the adsorption process, possibly due to the combination of electrostatic attraction between the dye molecules and the surface functional groups, in addition to adsorption in the pores of the material [14].

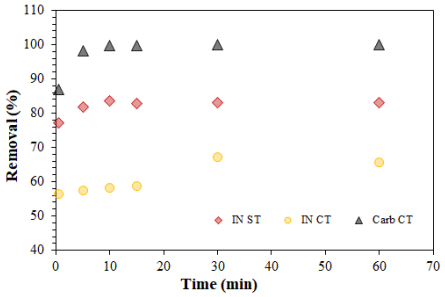

Fig. 2 MB removal percentage.

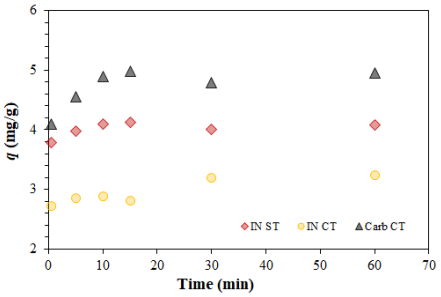

Fig. 3. Adsorption capacity profiles.

The experimental adsorption capacities at equilibrium, for the initial concentration of 50 mg L^{-1}, were 4.0 mg g^{-1} for IN ST, 3.2 mg g^{-1} for IN CT, and 4.79 mg g^{-1} for Carb CT, considering an equilibrium reached in 30 minutes.

Fig. 4 shows the pH variation profiles in relation to the initial pH. A pHpcz of 7.3 was obtained for IN ST, 4.5 for IN CT and 4.8 for Carb CT. The difference in the pHpcz of IN ST is due to the presence of intrinsic carbonate in the shrimp shell and, according to the literature on MB adsorption on biochars derived from crustaceans, an alkaline pH (around 11) has been identified as ideal to optimize the process of adsorption [9].

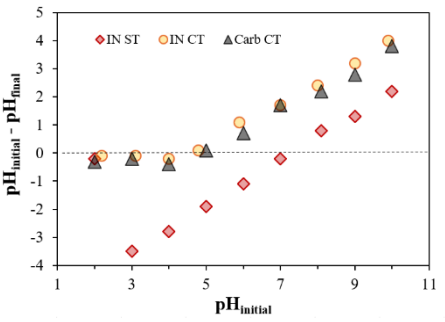

Fig 4. pH variation profiles of biosorbents.

It is believed that the superior performance of the calcined biochar compared to the in natura sample is due to the formation of micropores in the biochar structure, resulting from the presence of a non-inert medium that, in contact with the biomass degradation, created an environment rich in CO_2, acting as a physical activator during the thermal process.

4. Conclusion

This study explored the use of calcined shrimp shells for effective removal of methylene blue. The results highlighted its potential as an alternative adsorbent for the removal of dyes in aqueous matrices. However, further investigation is necessary regarding thermal treatment in a non-inert atmosphere for biomass. This method emerges as a promising solution to waste management challenges, promoting circular economy principles and enhancing global sustainability.

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