Valorization of blue crab (*Callinectes sapidus)* by-products as adsorbents

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Keywords: crab waste, pyrolysis process, carbonated materials, methylene blue

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ABSTRACT

Crustacean wastes are a good source of valuable nutrients and other bioactive compounds. They are usually not fully utilized but disposed of in the environment. Over the years, new processes of crustacean wastes have been developed leading to new innovative products such as functional food ingredients, medicines, cosmetic, feeds, fertilizers and adsorbents. Therefore, a crab waste utilization strategy would lead to the development of innovative high-added value products. The purpose of this research is the valorization of blue crab waste (*Callinectes sapidus)* to produce new carbonaceous materials with high adsorption capacity. The crabs were separated into shells (CCSS), pincers (CCSP), and legs (CCSL). The adsorption properties of the materials were investigated with methylene blue (MB) adsorption in aqueous solutions and their characterization with the FTIR analysis. The results have shown that the carbonaceous materials pyrolyzed at 800°C presented the maximum adsorption percentage according to the order: CCSL>CCSS>CCSP. The maximum adsorption in equilibrium is equal to 31.88 mg M.B/g of CCSL. The FT-IR spectra of the materials show a broad-band at 1623-1626 cm^{-1} probably due to C=C stretching "in plane" vibrations of the aromatic ring of MB. Such carbonaceous materials, derived from crab wastes, can be used as adsorbents, reducing pollutants in the marine ecosystem, as well as mitigating environmental pollution. One more benefit is the investment incentives to produce innovative carbonaceous materials for profit while contributing to the sustainability of the fisheries and aquacultures through the circular economy.

Keywords: blue crab biomass, methylene blue adsorption, carbonization, FTIR analysis

INTRODUCTION

The blue crab (B.C.) also known as *Callinectes sapidus* is an aboriginal crustacean from the western coasts of the Atlantic Ocean that has been adapted to the Mediterranean Sea (Mancinelli et al., 2017). In recent years there has been a rapid increase in crab consumption and annually more than 6 to 8 million tons of crustacean wastes are produced (Yan & Chen, 2015). Large quantities of crab waste are discarded in the soil environment (Gao et al., 2016b). Moreover, the crab waste is considered a cheap material because it is not fully utilized. Therefore, the valorization of crustacean biomass should be a priority due to their large abundance in nature. The crab waste utilization strategy could create benefits such as the mitigation of environmental pollution (Gao et al., 2016b). Particularly, the chemical composition of the crab waste shells is rich not only in calcium carbonate but also in chitin and chitosan. Also, the crab waste shells are rich in, $CaCO_3$, silica, and phosphates (Sebestyén et al., 2020). Industries, such as food and beverages, printing inks, textile, paper products, and leather, use different types of dyes to color their products. Therefore, the produced wastewater, containing a high level of dyes, is discharged into the environment without prior treatment. Dyes are organic compounds and are classified to natural and synthetic. Many of them are classified as hazardous materials with severe impact on human health. Many methods were applied to remove dyes from wastewater, i.e., electrochemical degradation, electrocoagulation, advanced oxidation, photocatalytic degradation and adsorption (Idohou et al., 2020). Adsorption is a low-cost method with high applicability.

Crab wastes can be converted to substantially more valuable products with the appropriate method such as bio-sorbents, templates for nanostructures, carbon sources of high-added value, or precursors for a calcium-rich biochar (Sebestyén et al., 2020). One common carbon production technique is the fast pyrolysis process, which produces biochar from wastes, and is considered an economical and environmentally friendly processing method for wastewater treatment (Hopkins et al., 2022). The development of innovative high added value products such as pyrolyzed or activated carbons happens due to the unique microstructure of the crab shell. An important characteristic of biochar is the high surface area, the large volume of pores and the surface functional groups. Pyrolyzed carbons can be applied as filters to purify water or to eliminate the removal of dyes from effluents to the environment through the adsorption process. In this study, crab wastes were used to produce new adsorbents via the pyrolysis process. The produced materials were characterized by FTIR analysis, and their adsorptive abilities were determined by the discoloring of a dye.

EXPERIMENTAL

Callinectes sapidus crabs were caught in the Missolonghi lagoon area (Klisova). After their transportation to the laboratory, the frozen crabs were thawed smoothly at room temperature. The crabs were rinsed with running water and then crab wastes were separated into shells (CCSS), pincers (CCSP), and legs (CCSL). Each crab waste sample was dried separately in an oven for 96 hours. The dried waste was crushed by a blender, grounded by a mortar, sieved up to 200μm, and then stored in a shady place at 20°C. The specimens were then carbonized in a horizontal cylindrical tube oven under a continuous flow of nitrogen at 800°C. The carbonaceous materials were weighted before and after the carbonization process.

The initial parameter, that characterizes the final carbonaceous material, is the weight loss percentage calculated measuring the weight of the crab waste before (B_o) and after (B) the carbonization process, $\%(B_o-B)/B_o$. This index indicates the successful carbonation of the materials.

The discoloring abilities of the carbonaceous materials were also determined. Methylene blue dye (MB) was produced in a solution of 0.032g/L. More specifically 0.015 g of each adsorbent were mixed with 15mL of dye and placed in test tubes in a proportion of 1g of adsorbent/L of dye. Then, the samples were stirred at 240 rpm for 12h at 20ºC and then were centrifuged for 5 min at 5000 rpm. The procedure was repeated every 12 h until the samples have completely discolored, and the absorbance values have stabilized. The absorbance of each sample was measured in the visible spectrophotometer ONDA V-10 Plus spectrophotometer (λ = 664 nm). The adsorbed amount (q_t) of the adsorbate onto the adsorbent was determined from the difference between the initial amount of adsorbate (q_o) in the solution and the measured amount of the adsorbate, expressed as % adsorption, i.e. $(q_t/q_o)\cdot 100$. The above procedure was repeated three times for each sample.

FT-IR spectra were determined for the carbonized biomass before and after methylene blue adsorption. An Agilent Cary 630 FTIR spectroscope, equipped with an ATR accessory, was used with Microlab software. All measurements were performed on the same day at 25◦C. The spectra were measured in the region from 400 to 4000 cm^{-1}. The diamond ATR sensor was cleaned with ethyl alcohol or acetone before each sample measurements.

RESULTS AND DISCUSSION

The weight loss percentage of each carbonaceous material after the pyrolysis process is shown in Figure 1. It seems that CCSL presents the highest weight loss while CCSS the lowest. The weight loss increased significantly on the materials CCSL and CCSP at 53% and 52.4%, respectively. The carbonaceous material derived from crab shell (CCSS) presents the lowest weight loss percentage (24%) due to the highest roughness of the raw material. According to literature (Lawtae and Tangsathitkulchai, 2021), the weight loss decreased rapidly in the temperature range from 250 to 400 °C due to the release of volatile substances caused by the decomposition of cellulose and hemicellulose. Then, for the temperatures above 400 °C, it seems a slow decrease in the remaining weight and finally approached a constant yield of solid char.

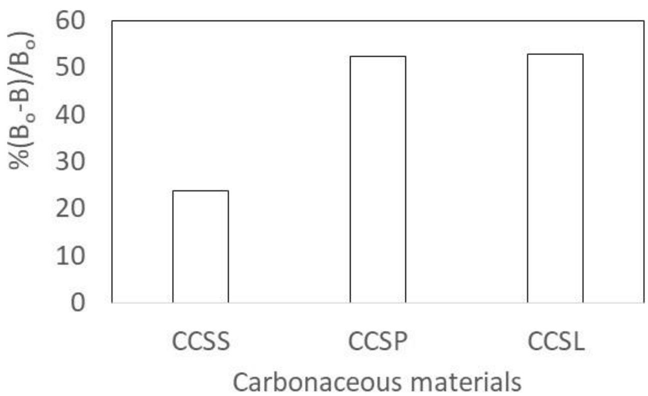
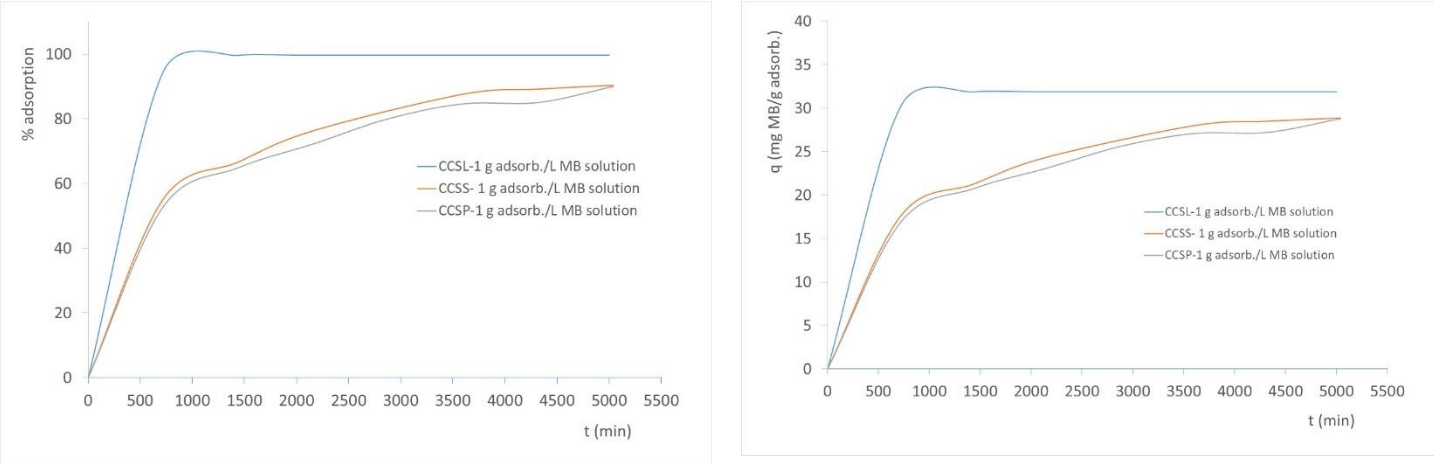


Figure 1: Percentage of weight loss for each sample after carbonization

The adsorption capacity of the samples can be observed in Fig. 2(a). The increase in MB adsorption follows the order: CCSL>CCSS>CCSP. The results have shown that the carbonaceous material derived from crab legs (CCSL) has a maximum MB adsorption equal to 99.64% compared to the other carbonaceous materials CCSS (90.30%) and CCSP (89.99%). Therefore, the carbonized crab legs adsorb quicker and higher amounts of MB dye in comparison with pincers and shells. The MB adsorption in equilibrium reaches after 10h for CCSL and after 83h for the other two materials CCSS and CCSP when the adsorbent to adsorbate rate is equal to 1g/L of MB.



(a) (b)

Figure 2: (a) Adsorption of methylene blue from aqueous solution on carbonaceous materials, (b) MB adsorption per gram of adsorbent versus time for the three carbonaceous materials (CCSL, CCSP, CCSS) in a proportion of adsorbent to adsorbate solution equal to 1/1 g/L

The MB adsorption per gram of adsorbent is presented in Figure 2(b). According to the results, it seems that MB adsorption follows the order: CCSL>CCSS>CCSP. The results have shown that the carbonaceous material derived from crab legs (CCSL) has the maximum MB adsorption in equilibrium equal to 31.88 mg M.B/g adsorbent compared to the other carbonaceous materials, i.e., 28.89 mg M.B/g of CCSS and 28.79 mg M.B/g of CCSP. Similar studies (Marrakchi et al., 2017) have shown a maximum MB adsorption equal to 184.40 mg/g of carbonized fishery waste. Fish scales were carbonized up to 600 °C then were impregnated by NaOH and finally were activated by heating up to 800 °C in N_2 atmosphere. Other studies have shown the use of carbonaceous materials derived from crab shell after pyrolysis process in N_2 atmosphere. It seems that the maximum adsorption of cationic malachite green and anionic Congo red was equal to 12.5 and 20.3 mg/g of adsorbent, respectively.

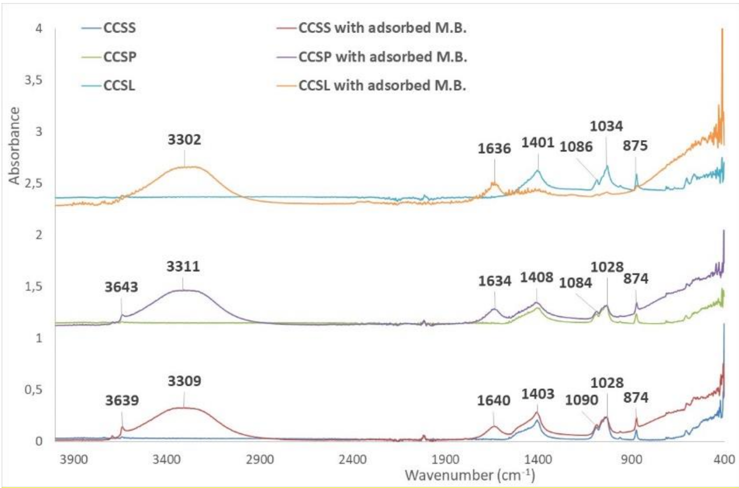


Figure 3: FTIR spectra of the carbonized biomass before and after MB adsorption.

To understand better the adsorption mechanism of MB on the surface of the produced carbonaceous materials, they were characterized with the FTIR analysis. All the materials were scanned in the region between 500 to 4000 cm^{-1} and the data are presented to Figure 3. An additional effect is that between the materials there is no displacement of the peaks, however some variations are distinguished in the intensities of the peaks before and after MB adsorption on adsorbents. The FT-IR spectra of the materials show a broad band around 3300-3310 cm^{-1} corresponding to O-H stretching vibrations, while the low peak at 3640 cm^{-1} corresponds to free -OH groups. Moreover, the peaks at 1623-1626 cm^{-1} may be attributed to C=C stretching "in plane" vibrations of the aromatic ring of MB. The bands at 1028-1034 cm^{-1} are assigned to -C-H bending "in plane" vibrations (Galletti et al., 2015). The peak at 875 cm^{-1} could be attributed to the out-of-plane bending vibration of C–H in the aromatic ring (Feng, 2020). The peaks at 1400-1410 cm^{-1} which is due mainly to the asymmetric deformations of C–H bonds, while the peak at 1080 cm^{-1} is due mainly to the stretching of C–O bonds (Soundhar & Kandasamy, 2019; Galletti et al., 2015). According to other studies (Liu et al., 2019), the FTIR analysis has shown the presence of MB peaks at 1600 cm^{-1} indicating the presence of aromatic C═C stretching vibrations. The adsorbent was banana pseudo-stem biochar which was prepared after the addition of anhydrous phosphomolybdic acid and then the pyrolysis process in a vacuum tube furnace at different temperatures under N_2 atmosphere. Although there are significant differences between the prepared materials and methods, the MB identification at a similar peak was presented.

CONCLUSION

- The blue crab wastes can be converted to carbonaceous materials via a pyrolysis process under an inert atmosphere, e.g. nitrogen atmosphere.
- They acquire high adsorption capacity in M.B dyes with no tendency to desorption. The increase in MB adsorption follows the order: CCSL>CCSS>CCSP.
- The MB adsorption in equilibrium reaches after 10h for CCSL and after 83h for the other two materials CCSS and CCSP when the adsorbent to adsorbate rate is equal to 1g/L of MB.
- According to FTIR analysis, the peak appeared at 1600 cm^{-1} shows the presence of C=C stretching "in plane" vibrations of the aromatic ring indicating the adsorption of MB to adsorbents
- One more benefit is the investment incentives to produce innovative carbonaceous materials for profit while contributing to the sustainability of the fisheries and aquacultures through the circular economy**.**

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