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

A. Zapantioti, I. Fotodimas, C. Gkaliouri, Z. Ioannou
Department of Food Science and Nutrition, University of the Aegean, Myrina, Lemnos, 81400, Greece

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

Presenting author email: zioan@teemail.gr

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).

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. 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).

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 MB dye.

Experimental

Callinectes sapidus crabs were caught in the Missolonghi lagoon area (Klisova). 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. The discoloring abilities of the carbonaceous materials were also determined using methylene blue dye (MB) in a concentration of 0.032g/L. 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. All measurements were performed on the same day at 25◦C.

Results & Discussion

CCSL presents the highest weight loss while CCSS the lowest (Fig.1). The weight loss increased significantly on the materials CCSL and CCSP at 53% and 52.4%, respectively. The increase in MB adsorption follows the order: CCSL>CCSS>CCSP (Fig.2). 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. According to Fig. 3, CCSL has the maximum MB adsorption in equilibrium equal to 31.88 mg M.B/g adsorbent compared to the other materials, i.e., 28.89 mg M.B/g of CCSS and 28.79 mg M.B/g of CCSP.

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} 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).

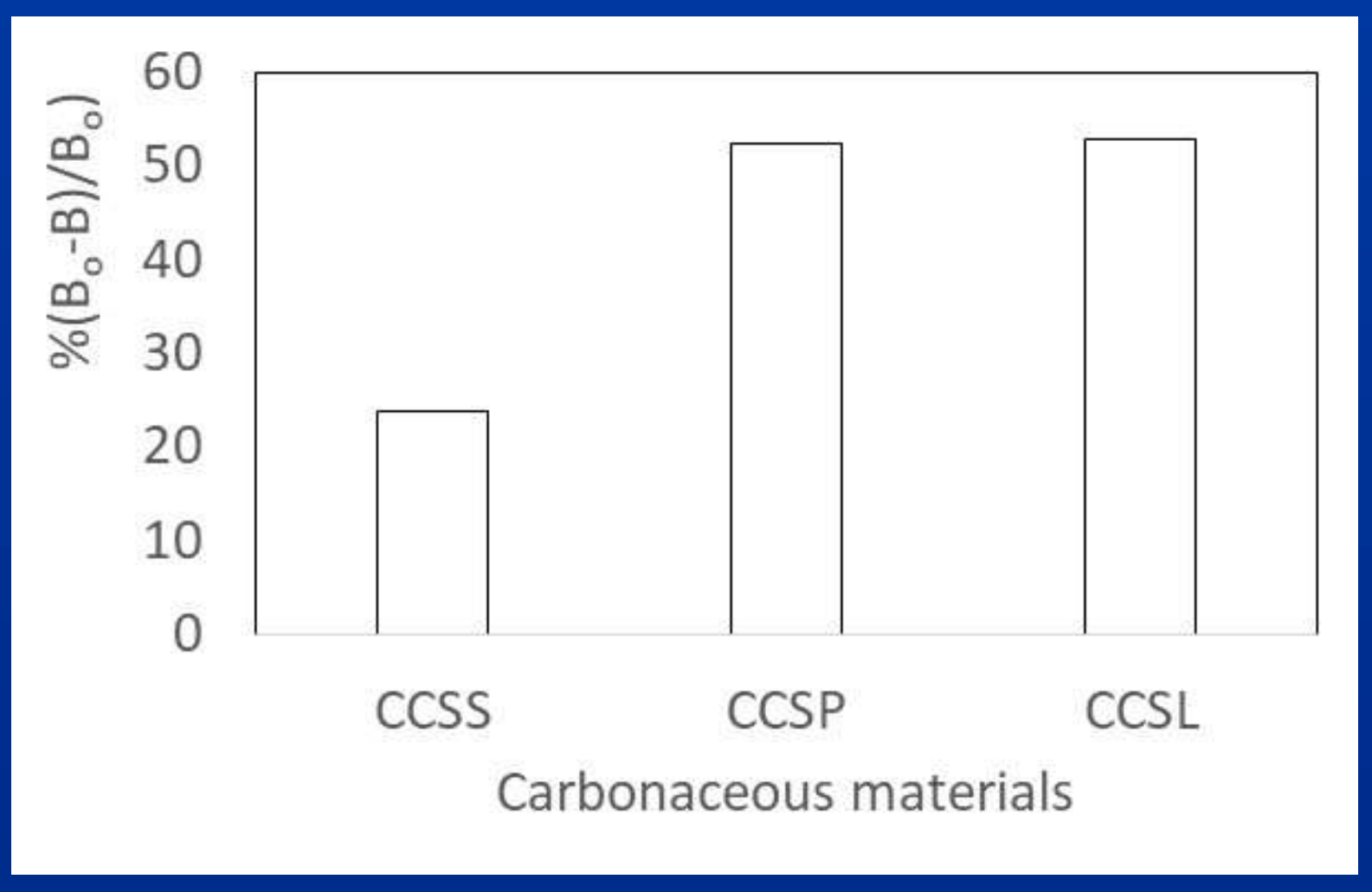

Fig 1: Percentage of weight loss for each sample after carbonization.

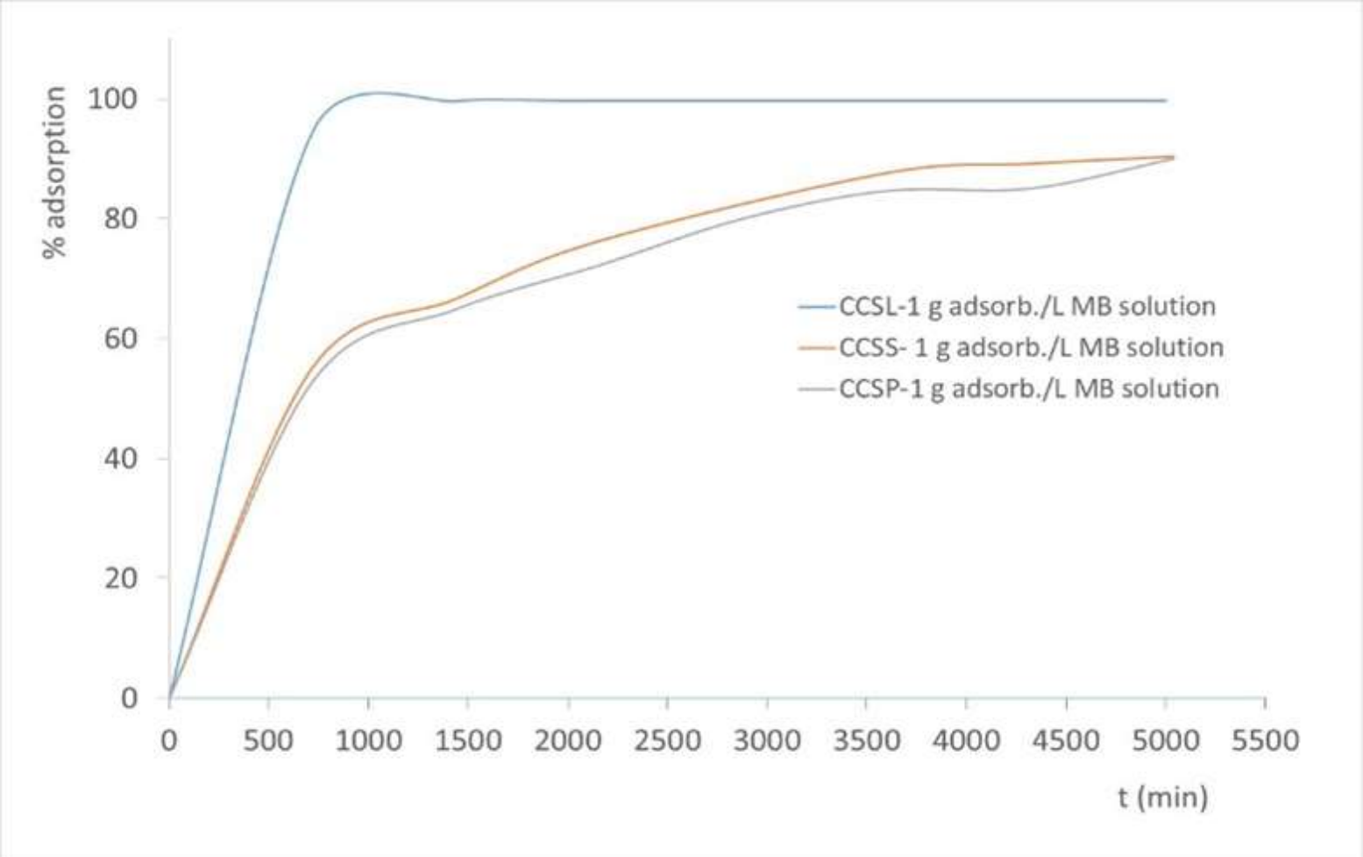

Fig 2: Adsorption of methylene blue from aqueous solution on carbonaceous materials.

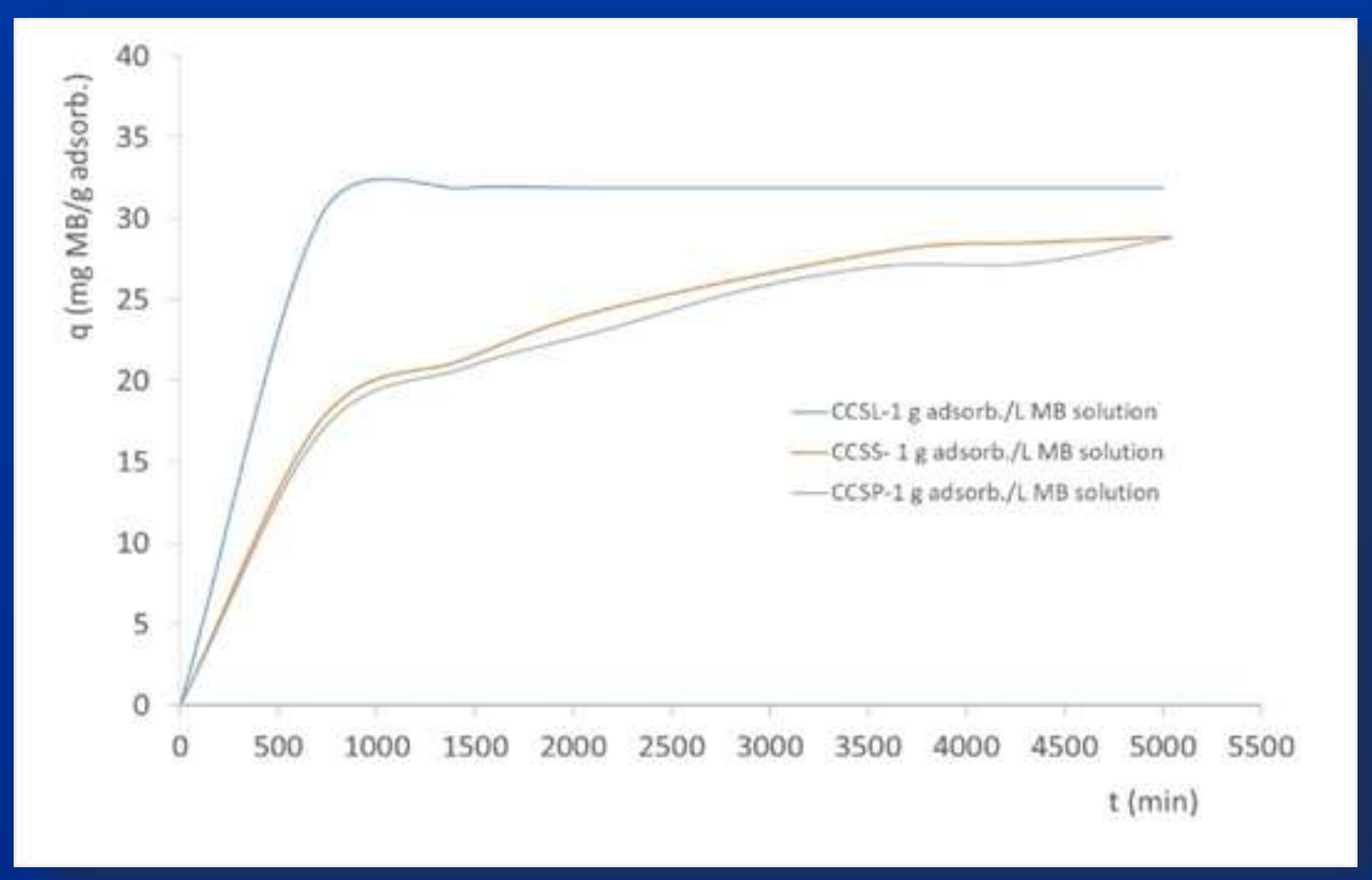

Fig 3: MB adsorption per gram of adsorbent versus time for the three carbonaceous materials.

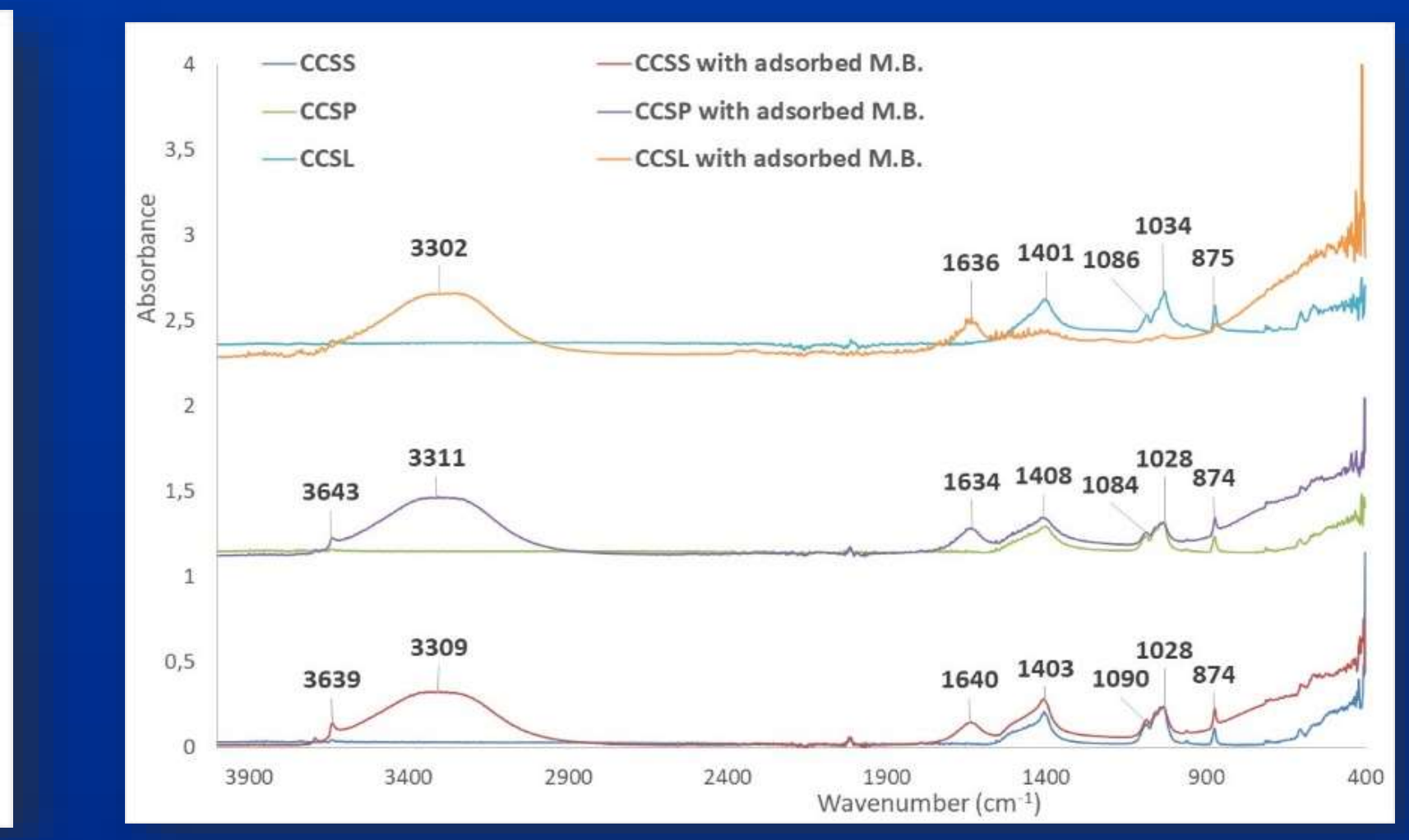

Fig 4: FTIR spectra of the carbonized biomass before and after MB adsorption..

Conclusions

- The blue crab wastes can be converted to carbonaceous materials via a pyrolysis process
- 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.
- 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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