SCIENTIFIC REPORT

Project title:
New composites based on carotenoid-depleted seafood shell waste with efficient environmental pollutants adsorption

Project code:
PN-III-P1-1.1-PD-2021-0477

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Project website: https://shellpolads.granturi.ubbcluj.ro

1. Introduction, background and current progress

Nested within the concepts of Blue bioeconomy and the circular economy, the purpose of this project is to explore if the locally sourced crustacean and bivalve shells can be redirected to pollutants adsorbent material production, rather than sending it to landfills together with other food waste. This project differentiates itself from usual adsorbent material testing by its scope: instead of limiting ourselves to adsorption tests alone, we aim to develop an integrated shell valorisation process from materials sourcing to post-adsorption handling.

Environmental pollution by pesticides is becoming an increasing global problem as a consequence of intensification of agriculture and their increased application. The situation is aggravated by the fact that agricultural and food production systems in less developed countries tends to be less regulated, thereby offsetting the efforts to limit harmful pesticide usage in developed countries (Hassaan et al., 2020).

One of the common mechanisms of pollutants removal from aqueous media is the usage of adsorbent materials, which feature large surface area and/or specific surface properties which allow the attachment of pollutant molecules and their physical removal together with the adsorbent material. Crustacean shells were considered as adsorbent materials by several research groups in the past, for removal of heavy metals, dyes, or other harmful compounds compounds (Morris et al., 2011; Fabbricino et al.,, 2016; Rissouli et al., 2017)). However, the mentioned studies are limited in scope of experimental approach usually only to testing of the absorption capacity, with no concrete consideration of material handling before and after the adsorption process.

On the other hand, in this project, we consider a broader context of circular economy and the blue bioeconomy, where the shells, a common food waste, are viewed as a secondary raw material with potential applications. Thus, we target the

production of adsorbent material from waste shells, but we also pay due consideration to the material preparation, its re-usability, and its handling after its useful (for adsorption) lifetime has run out. Turning powdered waste shells into a novel adsorbent material has the potential to solve several current problems:

- it would prevent landfill growth by redirecting the waste back into industrial circulation,
- it will be beneficial for human and environmental health by slowing down the growth of landfills and attached management costs,
- it would prevent unnecessary input of pristine materials into adsorbents production,
- it would further promote deep research into the blue bioeconomy, and ensure strengthened knowledge-based management.

These are only some of the few potential benefits. Surely there exist adsorbents obtained from other sources, some of which with even higher pore surface area than the shells derived from food waste, but we stress again the general interest in developing a complete and rounded, knowledge-based, processing method and application for different major types of waste items, to enable the above benefits and material circulation between the industries with minimal adverse consequences.

The current reporting period comprises the Objective 1: Obtaining of novel adsorbent micropowder from biomineral waste materiall, that was fully achieved. All the three activities were completed, and all the deliverables have been achieved. The results of the activities 1.1., 1.2. and 1.3 and the deliverables are presented below.

2. Progress on activities and their results

- Activity 1.1. Analysis of crab shell material before and after carotenoids extraction by X-ray diffraction, SEM, EDX, BET, solid state NMR and Raman spectroscopy and DT/TGA to prospect if extraction induces chemical or structural changes.
- Activity 1.2. Analysis of waste bivalve shells by X-ray diffraction, SEM, EDX, BET, solid state NMR and Raman spectroscopy and DT/TGA to establish the suitability and methods for obtaining novel adsorbent material

2.1. The samples and their preparation

The shells of the Atlantic blue crab (*Callinectes sapidus*) and the Spider crab (*Maja squinado*) were obtained as fisheries by-catch waste from an authorised fisheries inspector. Shells of the Spiny lobster (*Palinurus elephas*) were obtained from a restaurant as food preparation waste. All shells used here were thoroughly cleaned with water and dried at room temperature. Bivalves, the oyster (*Ostrea edulis*) and the mussel (*Mytilus galloprovincialis*) shells were obtained from a shellfish hatchery of the university of Dubrovnik.

The crustacean shells were subjected to carotenoids extraction. This was done by 24 hour immersion method involving shell fragment in acetone, described in more

detail in Nekvapil et al. (manuscript in preparation). Figure 1 shows the visual shell aspect before and after orange/red carotenoids extraction.

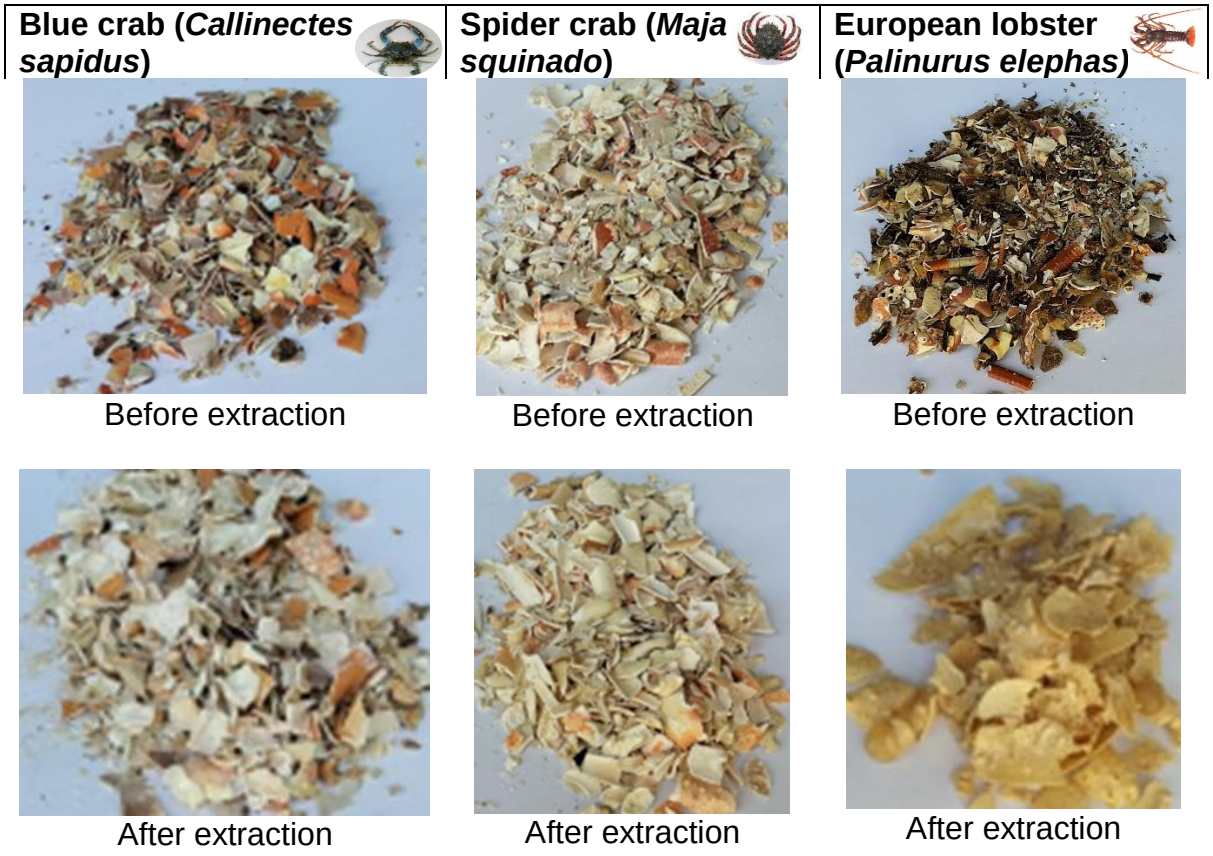


Figure 1. Visual aspect of the shells of three crustacean species considered in this project.

Extracted and native shells were subsequently milled in a Retsch vibratory disc mill, with a single 20-second cycle. In addition to crustacean shells, shells of two bivalve species were used as unrelated references. There are no extractable pigments in bivalve shells, hence they were ground to powder without the extraction step. The powders obtained from native crustacean shells were orange in colour, while those from post-extraction shells and bivalve shells was white, consistent with predominantly calcite composition.

2.2. The analysis of crab shell material and waste bivalve shells

2.2.1. SEM – scanning electron microscopy

Bulk shells feature a nanoporous structure, which is also transferred to the powder obtained by milling of respective shells (Nekvapil et al., 2019). According to several recent studies including milling of blue crab shells (Nekvapil et al., 2019; Nekvapil et al., 2021; Ogresta et al., 2021), the particles` size may be influenced by prior treatment of shells, but the diameter of the majority of particles is below 100 µm. To visualize the shell powder particles` nanomorphology, scanning electron

microscopy was employed here. The powder particles obtained from the post-extraction shells do not seem much different in terms of morphology than those obtained from native shells. However, it is evident that the particles feature an extensive roughened surface, which presumably represents the remnant of the bulk nanochannel network. Difficulty to focus on the biogenic powder particles under high- was also noted in Nekvapil et al. (2019). Figure 2 shows the SEM micrographs of the crustacean shells before and after extraction.

EDX was also attempted, however, due to its low precision regarding light elements, it showed signals of Ca, C, O, Mg and occasionally P and K, which are already known components of the shell (Nekvapil et al., 2020), and with no consistent differences between native and post-extraction material., which are already known components of the shell (Nekvapil et al., 2020).

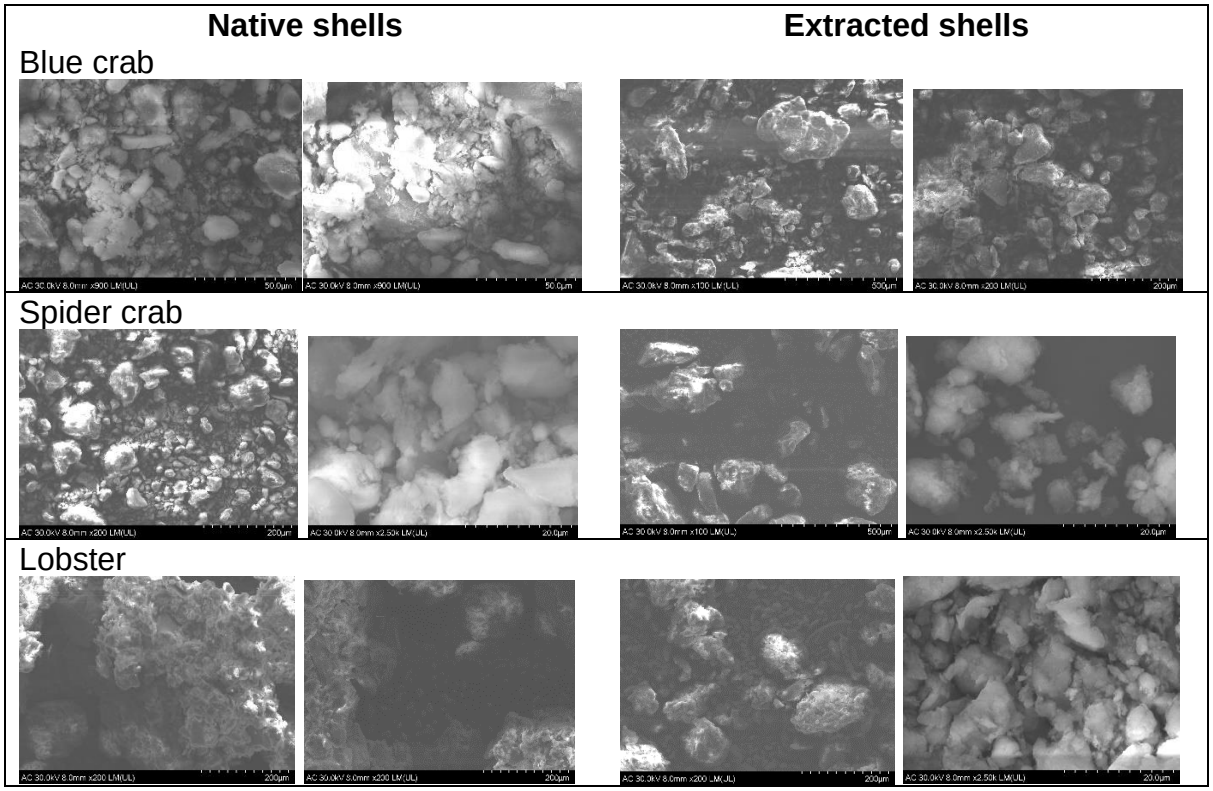
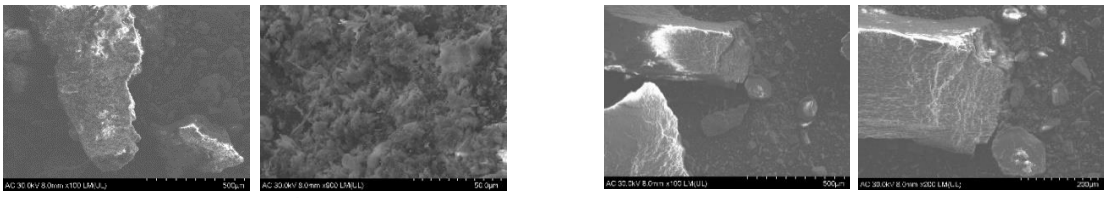


Figure 2. SEM images of the crustacean biogenic powder particles, obtained by milling of shell fragments from the same stocks before and after extraction.

The oyster and mussel shells also feature a roughened surface, however, their porosity is questionable, as bivalve shells feature more of a compact, layered shell structure (Figure 3).



Mussel Oyster

Figure 3. SEM images of powder particles obtained by milling of mussel and oystr shells.

The extraction with acetone does cause the co-extraction of lipids (and other compounds) alongside carotenoids. Comparative SEM analysis of the pores in the bulk native and the post-extraction shells revealed no notable difference in the aspect of the shell surface, cross-section and the pores (Figure 4).

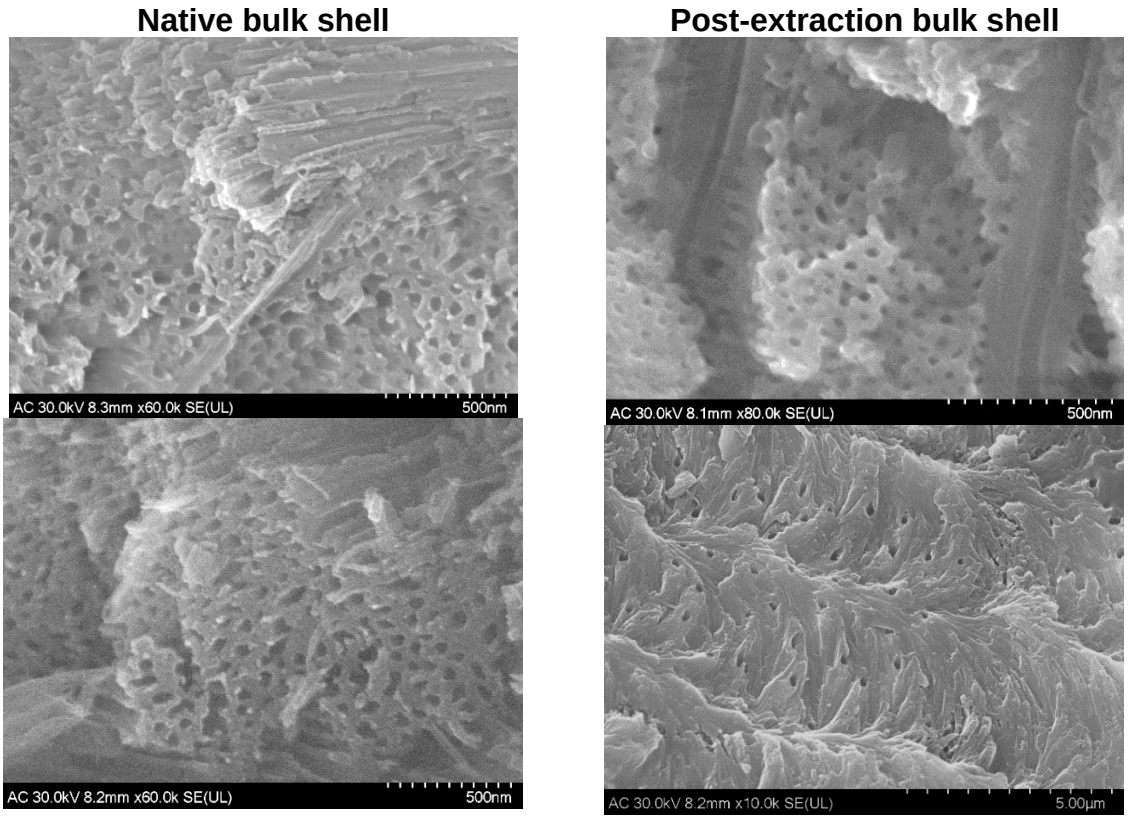


Figure 4. Comparative display of the bulk shell morphology of native and post-extraction shell, viewed under SEM.

2.2.2. XRD – x-ray diffraction

Consistently with previous reports (Nekvapil et al., 2020; Ogresta et al., 2021), the crustacean shells were shown to consist of magnesian calcite (Mg-calcite) and α-chitin as the dominant mineral phases (Figure 5). The same phases were also observed in the material after carotenoids extraction was conducted. In lobster shell, the monohydrocalcite phase was additionally observed in post-extraction shells. This this $CaCO_3$ polymorph does not occur naturally in the shells, however, it was previously reported in shells kept in freezers (Ogresta et al., 2021), although, it is not clear under which exactly shell storage conditions it forms. It was not.

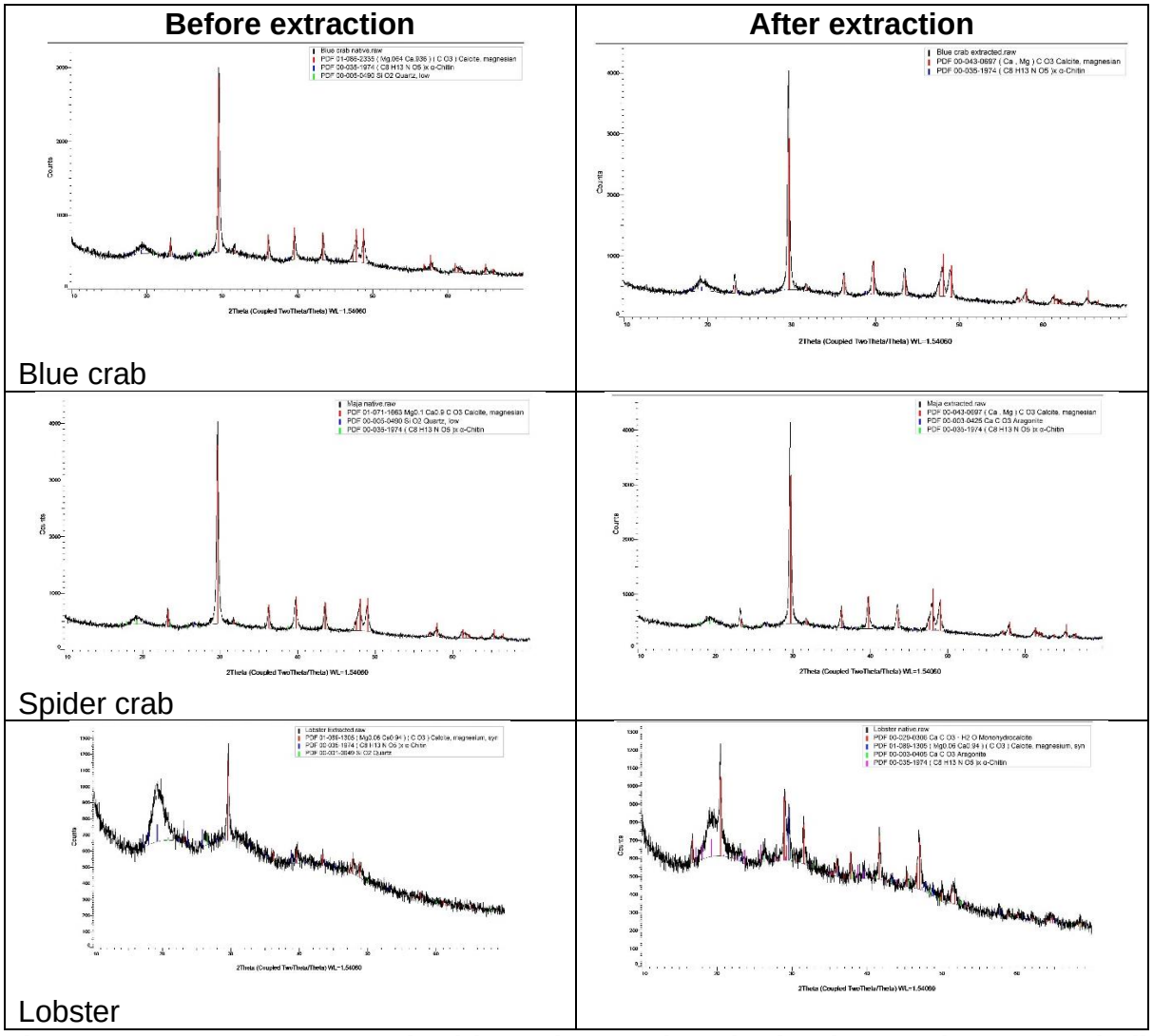


Figure 5. XRD patterns of the biogenic powder obtained from the same shell stock milled before and after acetone extraction of carotenoids.

The XRD patterns featured only reflection peaks of calcite in the case of oyster shell powder, and of calcite and aragonite in the case of mussel shells.

2.2.3. BET – nitrogen physisorption

Powder obtained from blue crab and spider crab post-extraction shells feature up to 10 times greater specific BET surface area than their native counterparts (Table 1). The reason for this may be the dissolution of lipids and denaturation of certain proteins, and consequent eliberation of pores. Significant differences between the respective values for shell powder and bulk shells may be explained by the fact that BET measurements refer to the pore wall surfaces, but not also to particle surface area.

Difficulties were encountered in thermal pre-treatment of lobster shells – probably the organic fraction in the shell is too great, which makes the proper sample preparation unfeasible, and consequently the measurements results are not relevant.

The lack of BET surface area and internal pore volume in the bivalve shells (oyster and mussel) indicates that their structure is indeed layered only, and not also nanoporous. There are not many literature reports employing BET to measure oyster shell porosity; nevertheless, Inthapanya et al. (2019) characterizedusing the powder from another oyster species, *Crassostrea gigas* using BET, as having the pore surface area of 1.910 m^2 g^{-1}. The cited value is still small, and the difference relative to our result can be attributed to different oyster species considered in the cited study and here. Likewise, the powder particles shown in SEM images of the above study (Inthapanya et al., 2019) are similar in surface morphology as the ones shown here. Xu et al. (2019) reported „oyster" powder surface area at 2.13 m^2 g^{-1}, however, the experimental approach was poorly described and the oyster species was not indicated, hence this information is of little utility here. We have submitted our oyster powder (species *Ostrea edulis*) powder which had initially no surface area to another BET analysis after treatment at 800 °C in air for 2 hours, and it still had no pore surface area measurable by this method.

Table 1. BET results on pore volume and diameter in biogenic powders obtained from native shells and crustacean shells after extraction.

Sample	[a]S_{BET} (m^2/g)	[b]V_p (cm^3/g)
Blue crab, before extraction	8.21	0.029
Blue crab, after extraction	32.94	0.078
Blue crab, native, bulk shell	23.46	0.036
Blue crab, post-extraction, bulk shell	22.17	0.028
Spider crab, before extraction	3.18	0.029
Spider crab, after extraction	32.57	0.086
Spiny lobster, before extraction	0	0
Spiny lobster, after extraction	1.38	0.010
Mediterranean mussel	0	0
European flat oyster	0	0

[a]S_{BET} – BET surface area; [b]V_p – pore volume.

2.2.4. TGA – thermogravimetric analysis

Thermogravimetric analysis was conducted to reveal the temperature steps at which certain shell constituents may be removed by volatilization. Two principal mass loss events could be observed from TG curves in our samples (Table 2; Figure 6) which also roughly correspond to the observed events by Nekvapil et al. (2019): (1) cca. 260 – 370 °C corresponding to decomposition of chitin and other organic

components, where crustacean shells lost about 20 to 25 % of weight, and (2) cca. 620 – 720 °C corresponding to decarboxylation of $CaCO_3$, where crustacean shells lost additional ~20 % of mass.

Bivalve shells, on the other hand, which are almost exclusively CaCO3, exhibited greater intensity of CaCO3 decarboxylation, losing 40 % of mass,; this observation is consistent with the report of Lee et al. (2019) In the case of mussel, decomposition of organic material represented only 3 % of mass, while in oyster this event was not observed at all. The events < 250 °C presumably correspond to evaporation of structural water.

Table 2. TGA results obtained on biogenic crustacean and bivalve shell powders air, heated from 100 to 1100 °C with temperature ramp of 10 °C/min.

Shell	State	1st interval (°C)	Starting and ending mass (%)	2nd interval (°C)	Starting and ending mass (%)
Blue crab	Native	260 - 370	87 – 67	620 - 720	59 – 40
	Post-extr.	260 - 370	89 - 69	620 - 720	62 – 41
Spider crab	Native	260 - 370	96 - 74	620 - 740	67 – 46
	Post-extr.	260 - 371	89 - 69	620 - 760	61 – 40
Lobster	Native	260 - 370	81 - 59	620 - 700	39 – 26
	Post-extr.	250 - 370	84 - 57	620 - 730	40 - 24
Oyster	Native			620 - 770	104 - 64
Mussel	Native	240 - 370	99 - 96	610 - 780	96 - 56

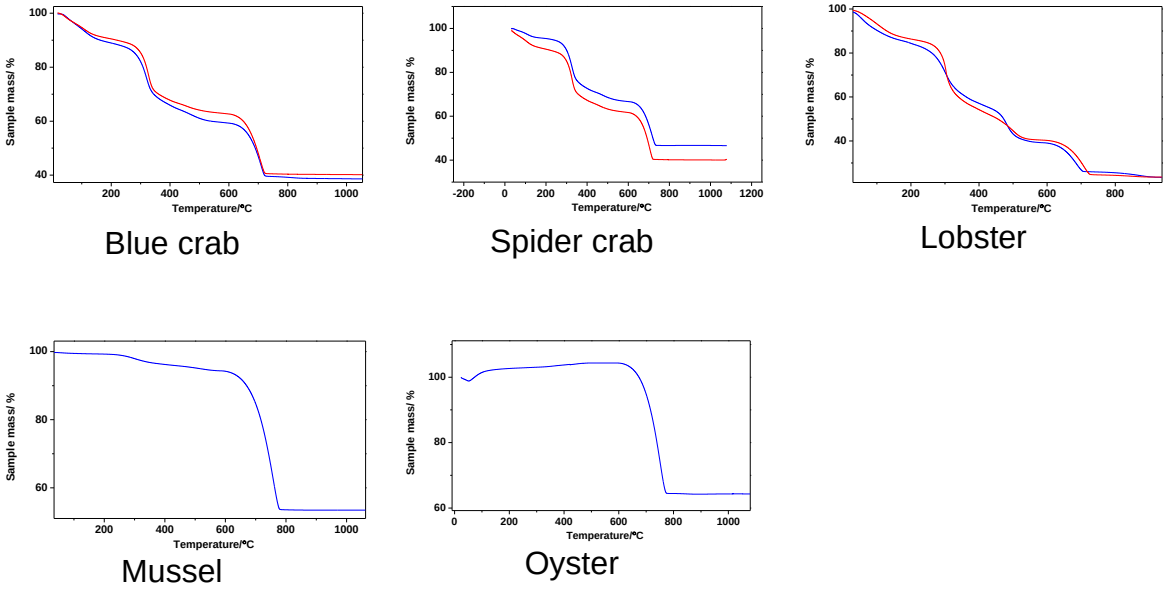
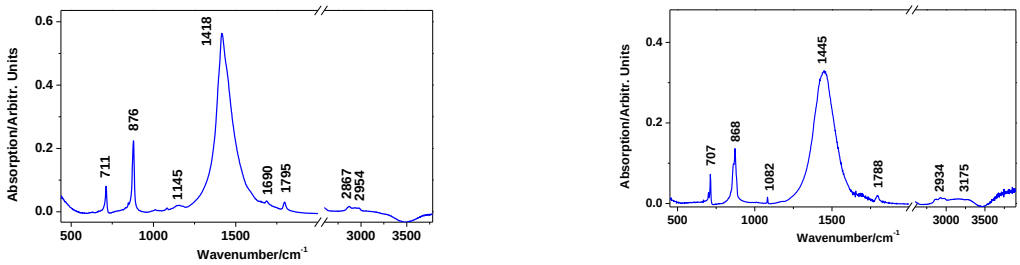


Figure 6. TGA curves obtained from biogenic crustacean and bivalve shell powder, in air, heated from 100 to 1100 °C with temperature ramp of 10 °C/min. Red = native shell, Blue = post-extraction shell. Note: bivalves (mussel and oyster) were not extracted, thus the curves refer to untreated shell powder.

2.2.5. FTIR (Fourier-transform infrared) spectroscopy

Soild-state NMR analysis was originally planned, however, in ulterior discussion with experts in the field, and following some of the findings within a previous study where the Project leader has participated (Ogresta et al., 2021), it was concluded that NMR analysis would not bring meaningful insights for our current objective. To compensate for avoiding NMR, we conducted FTIR and Raman spectroscopy analysis, where the Project leader is much more adept. FTIR was revealed to be a great substitute, showing major differences between native and post-extraction material.

Oyster and mussel shells lend themselves as a good case for facilitation of band assignments, as oyster shell consists exclusively of crystalline calcite, while mussel shell features a mixture of calcite and aragonite (Figure 7, Figure 8). Both of them feature negligible amounts of organic component. Aragonite and calcite are two polymorphs of calcium carbonate which feature slightly different spatial orientation of the CO_3^{2-} ion in the lattice, and hence slight shift in band positions are expected. Firstly, the sharp bands at 868-875 and 708-711 cm^{-1} are assigned to $v_{2\ asym}(CO_3^{2-})$ and $v_{4\ asym}(CO_3^{2-})$, respectively. The $v_{3\ asym}$ has two components, with v3a being strong in calcitic oyster, at 1418 cm^{-1}, and v_3b being strong in mussel, at 1445 cm^{-1}.

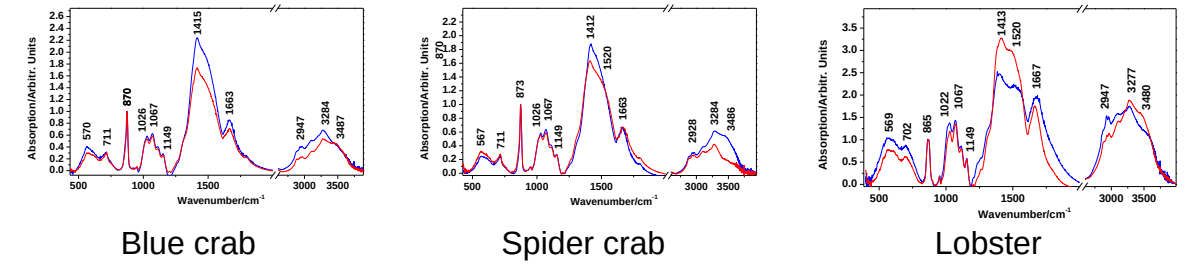


Oyster Mussel

Figure 7. FTIR spectra of oyster and mussel shell powder.

Results obtained on blue crab and spider crab shell powder exhibited a usual band configuration characteristic to shell waste (Ogresta et al. 2021). The spectra featured two main components: (1) the $CaCO_3$ signal (consider oyster signal) and (2) signal of protein-chitin organic component around 570, 1026, 1067, 1149 and 1667 cm^{-1}. The bands in 2800 – 3200 cm^{-1} may arise from any number of biomolecules with $CH_{2,3}$ groups, while the band around 3480 cm^{-1} is assigned to -OH vibration, presumably from structural water. One more wide organic feature around 1580 cm^{-1}, assigned to Amide II moiety, is hidden in the 1200 – 1700 cm^{-1} range. It is important to note that the respective range is composed of at least 4 considerably overlapping bands, and its proper analysis requires careful Lorentzian deconvolution and band area ratios consideration. There were no unambiguous signs of lipids.

FTIR Spectra from the shells were normalized to calcite band around 870 cm^{-1} to allow semi-quantitative comparison of powdered shell chemical composition of native and post-extraction shells. Except for $CaCO_3$ bands, which are considered here as unaffected (internal reference), bands with almost exclusive chitin contribution at 570, 1026, 1063 cm^{-1} seem unaffected. However, the CH2,3 bands, and the band around 1667 cm^{-1} with significant amide I moiety contribution and the hidden amide II band around 1580 cm^{-1} seem to have dropped in intensity, indicating the loss of some organic material during the extraction. This observation is consistent across all tested crustacean shells.



Blue crab Spider crab Lobster

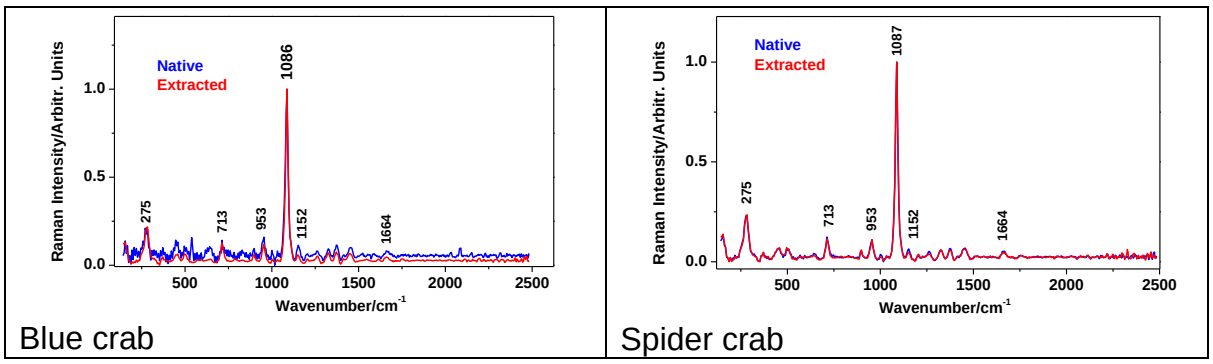
Blue line = native shells ; Red line = extracted shells

Figure 8. FTIR spectra of biogenic powders obtained by milling of crustacean shells from the same stock before and after extraction.

2.2.6. Raman spectroscopy

Raman spectra of the crab species show the signal of calcite, with the bands at 275, 713 and 1086 cm^{-1} (Behrens et al., 1995). The bands at < 953 and 1152 cm^{-1} represent the skeletal vibrations of chitin, the band at 1664 cm^{-1} its amide I groups, and the bands in 1200-1500 cm^{-1} its C-H modes. The bands of other compounds (proteins) are not clearly visible) (Figure 9).

The Raman spectrum of the lobster shell is of low quality, however, the band of monohydroxycalcite (MHC) is observed at 1067 cm^{-1}. The Raman spectrum of oyster shows exclusively bands of calcite, while the spectrum of the mussel shell shows a mixture of calcite and aragonite contributions.



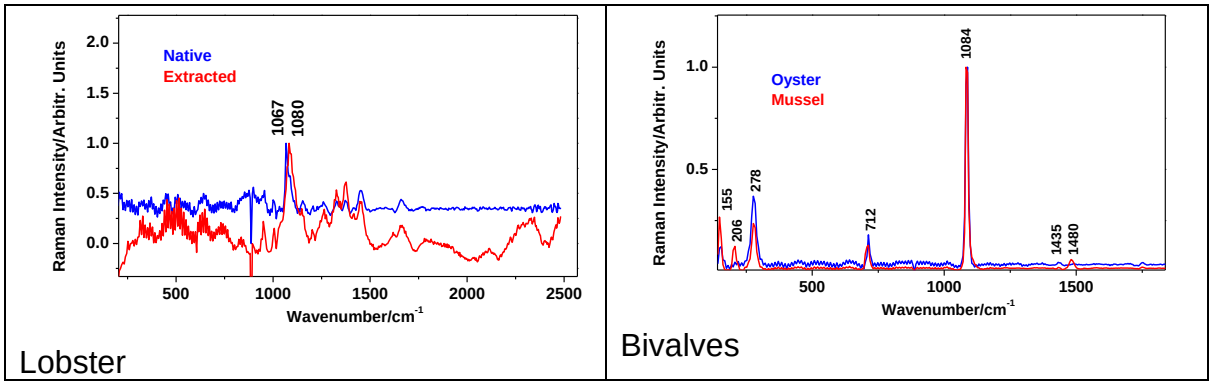


Figure 9. Raman spectra of the biogenic powders obtained from crustacean and bivalve shell powder. Spectra are normalized to the CO_3^{2-} stretching band at 1084 - 1086 cm^{-1}.

Conclusions

Connecting the results obtained from SEM, FTIR and BET (sharper visibility of particle nanomorphology, reduced lipid-related bands, and larger pore surface area and volume, respectively), we can conclude that acetone immersion for 9 to 24 hours causes the dissolution and removal of lipids located presumably inside the pores and crevices in shell structure. On the other hand, the rigid shell components, such as Mg-calcite biomineral and chitin scaffold remain largely unchanged.

Consequently, the results indicate that the carotenoids extraction step from crustacean shells is beneficial to the current aim, as it allows obtaining, on one hand, valuable carotenoids and, on the other hand, increased surface area of pores available for pollutant adsorption.

2.3. Activity 1.3.

- conducting thermal treatment of the porous shell material following the conclusions of Activities 1.1. and 1.2., obtaining of microparticles with potential adsorption capability.

Above comparative analysis has shown that the powdered shells of the blue crab (*Callinectes sapidus*) and the spider crab (*Maja squinado*) are similar to each other in properties relevant for the current study, as are also oyster (*Ostrea edulis*) and mussel (*Mytilus galloprovincialis*). Lobster (*Palinurus elephas*) shells gave the worst results of all crustaceans in BET analysis and lowest calcite crystallinity, these shells were not considered further. Thus, the blue crab and oyster shells will be used for the next studies.

2.3.1 Thermal treatment and attempts to increase the biogenic nanoporous powder pore surface area

Thermal treatments of the shells at over 400 °C were conducted at each trial in order to burn off chitin and obtain $CaCO_3$-only powder. Calcinations were run both in air and in inert argon atmosphere for greater control over the experimental conditions.

The TGA curves in argon atmosphere are curiously similar to those in air (Figure 10, Table 3), which indicates that the decomposition of the shell constituents is conditioned by the temperature, but the reaction mechanisms may be different in the two cases. Indeed, bulk decomposition of chitin from crab shells occurs between 246 and 360 °C in both dynamic air and inert atmosphere (nitrogen), although the finer scale kinetics is dependent on the deacetylation degree of the sample and the atmosphere used (Barbosa et al., 2019; Koll et al., 1991). Also, the volatilization mechanisms are different, with carbon dioxide, carbon monoxide and ammonia being the possible degradation products of crab shell chitin in dynamic air (Barbosa et al., 2019), and acetamide, acetic acid and other minor products recoded during thermal decomposition in argon atmosphere (Koll et al., 1991).

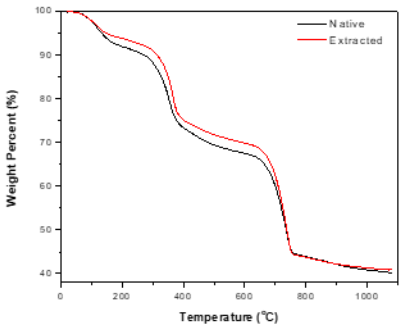


Table 3. Thermal intervals of major mass loss in blue crab shell powder calcinated in argon.

Sample	Interval (°C)	Mass (%)	Interval (°C)	Mass (%)
Native	125 – 385	96 – 74	625 - 755	67 - 45
Post-extraction	125 - 385	96 – 76.5	625 – 755	69 - 45

Figure 10. TGA curves of blue crab shell powder calcinated in argon; blue = native shells, red = post-extraction shells.

Although the TGA curves indeed look similar, FTIR detected subtle differences between the two treatments. Namely, the shell powder treated in argon exhibits significantly lower CO_3^{2-} asymmetric stretch bands at around 1420 and 1480 cm^{-1}, with concommitant presence of the prominent C-H stretching mode at 2894 cm^{-1} and an even stronger band at 3407 cm^{-1} (Figure 11). According to general vibrational spectroscopy considerations (Smith, 2019; Smith and Dent, 2005), and considering the expectations from the sample, the presumable assignment of the latter band is N-H stretching from nitrogenous compounds left after anoxic degradation of chitin.

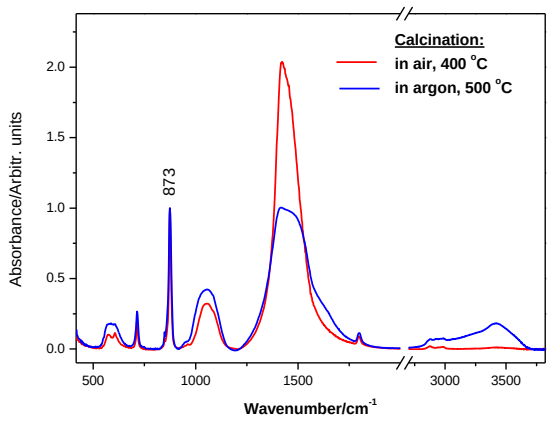


Figure 11. Comparative display of FTIR spectra of post-extraction blue crab biogenic shell powder calcinated in air and in argon.

Because thermal treatment only (either in air or in argon) did not result in higher porosity values than those measured in post-extraction shells, the powder was additionally exposed to mild acids and bases for hourly intervals, followed by washing in distilled water, drying and finally BET analysis to reveal if the treatments modified the porosity (Figure 12).

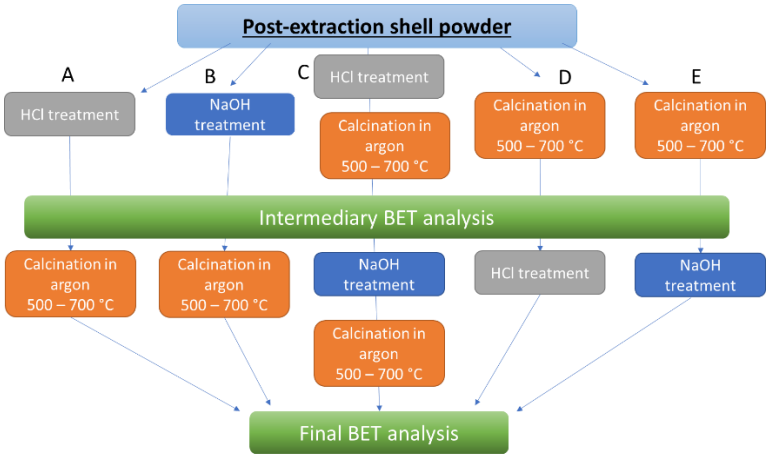


Figure 12. Schematic presentation of the general biogenic shell powder treatments conducted to attempt to increase the pore surface area. Each pathway contained several runs with varying treatment details.

The experiments conducted for this activity provided a lot of observations: for instance, if too strong acids were used, the $CaCO_3$ shell powder used to be „eaten away" leaving residues with several-fold smaller volume than the starting material, which was often too low sample quantity even for BET analysis.

The most effective treatment (in the sense of increasing pore surface area) was achieved with blue crab shell using the pathway C (Figure 6), and involved both acid and base treatment, and two calcination steps. This way the pore surface area was increased from initially 32.94 $m^2\ g^{-1}$ to 250.38 $m^2\ g^{-1}$. Treatments involving only acid or only base treatment did not result in higher pore surface area than the starting material.

Finally, it should be noted that we will establish a method for obtaining the adsorbent material which has the gratest power to increase the pore surface area. However, due to the natural origin of the material, it is not possible to guarantee which will be the final value of the surface area, and quantify to what extent did our method contribute to its increase. The issue of inter-sample differences in crustacean shell biogenic material was explored in detail in the publications by Nekvapil et al. (2020) and Ogresta et al. (2021)(information contained in the Supplementary material accompanying the article and held by the authors). Hence, it results that, when handling this type of samples (crab shell derivatives), it is more important to develop a robust analytical/processing methods rather than attempting to obtain specific experimental values.

The milestones were achieved:

- method for obtaining the adsorbent material from waste crab shells through chemical and thermal treatment
- method for obtaining the adsorbent material from waste bivalve shells through mechanical processing

3. Dissemination – conference

The results were presented through two oral presentations at one international conference:

Conference homepage: www.icpam.ro

Conference programme: https://icpam.ro/programme-icpam/ (presentations on 10.9.2022 at 19:00 and 14.9.2022 at 18:00)

Oral presentation 1
Title: Screening of waste shell biomaterials for recycling as adsorbents for water-borne pollutants
Authors: F. Nekvapil, G. Lazar, M-L. Soran, M. Mihet, R. Hirian, A. Ciorita, S.B. Angyus, T. Kusovac, M. Precanica, S. Tomšić, B. Glamuzina, S. Cînta Pinzaru

Conference: 14th International Conference on Physics of Advanced Materials (ICPAM-14), held in Dubrovnik (8.-15. September 2022)

Oral presentation 2
Title: Innovative biofertilizer from two aquatic waste materials and its influence on carotenoid content in lettuce crop
Authors: F. Nekvapil, G. Lazar, R. Hirian, M. Aluas, M. Suciu, T. Tamaș, L. Barbu-Tudoran, S. Tomšić, B. Glamuzina, S. Cînta Pinzaru
Conference: 14th International Conference on Physics of Advanced Materials (ICPAM-14), held in Dubrovnik (8.-15. September 2022)

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References

Assunta Pisu, F., Chiriu, D., Ricci, P.C., Carbonaro, C.M. Defect Related Emission in Calcium Hydroxide: The Controversial Band at 780 cm−1. Crystals 2020, 10: 266.

Barbosa, H.F.G., Francisco, D.S., Ferreira, A.P.G., Cavalheiro, E.T.G. A new look towards the thermal decomposition of chitins and chitosans with different degrees of deacetylation by coupled TG-FTIR. *Carbohydrate Polymers* 2019, 225: 115232.

Gesa Behrens , Liisa T. Kuhn , Rick Ubic & Arthur H. Heuer (1995):Raman Spectra of Vateritic Calcium Carbonate, Spectroscopy Letters: An InternationalJournal for Rapid Communication, 28:6, 983-995

Cheng, L., Wang, L. & Karlsson, A. M. Image analyses of two crustacean exoskeletons and implications of the exoskeletal microstructure on the mechanical behaviour. J. Mater. Res. 23, 2854–2872 (2008).

Fabbricino, M., Pontoni, L. Use of non-treated shrimp-shells for textile dye removal from wastewater. *J. Environ. Chem. Eng.* 2016, 4: 4100-4106.

Hassaan, M., El Nemr, A. Pesticides pollution: Classifications, human health impact, extraction and treatment techniques. *Egypt. J. Aquat. Res.* 2020, 46: 207-220.

Inthapanya, X., Wu, S., Han, Z., Zheng, G., Wu, M., Yang, C. Adsorptive removal of anionic dye using calcined oyster shells: isotherms, kinetics, and thermodynamic. *Environ. Sci. Pol. Res.* 2019, 26: 5944-4954.

Koll, P., Borchers, G., Metzger, J.O. Thermal degradation of chitin and cellulose.*J. Anal. Appl. Ppyrolysis* 1991, 19: 119-129.

Lazar, G., Nekvapil, F., Hirian, R., Glamuzina, B., Tămaș, T., Cîntă Pinzaru, S. Novel Drug Carrier: 5-Fluorouracil Formulation in Nanoporous Biogenic Mg-calcite from Blue Crab Shells←Proof of Concept. ACS Omega 2021, 6: 27781-27790. DOI: 10.1021/acsomega.1c03285.

Lee, J-I., Kang, J-K., Oh, J-S., Yoo, S-C., Lee, C-G., Jho, E.H., Park, S-J. New insight to the use of oyster shell for removing phosphorus from aqueous solutions and fertilizing rice growth. *J. Cleaner Production* 2019, 328: 129536.

Morris, A., Sneddon, J. Use of Crustacean Shells for Uptake and Removal of Metal Ions in Solution. *Appl. Spectrosc. Rev.* 2011, 46: 242-250.

Nekvapil, F., Aluas, M., Barbu-Tudoran, L., Suciu, M., Bortnic, R-A, Glamuzina, B., Cintă Pinzaru, S. From Blue Bioeconomy toward Circular Economy through High-Sensitivity Analytical Research on Waste Blue Crab Shells. ACS Sustainable Chem. Eng. 2019, 7: 16820-16827. DOI: 10.1021/acssuschemeng.9b04362.

Nekvapil, F., Cintă Pinzaru, S., Barbu-Tudoran, L., Suciu, M., Glamuzina, B., Tamaș, T., Chiș, V. Color-specific porosity in double pigmented natural 3d-nanoarchitectures of blue crab shell. Sci. Rep.-UK 2020, 10: 3019. DOI: 10.1038/s41598-020-60031-4.

Nekvapil, F., Glamuzina, B., Barbu-Tudoran, L., Suciu, M., Tamas, T., Cinta Pinzaru, S. Promoting hidden natural design templates in wasted shells of the mantis shrimp into valuable biogenic composite. Spectrochim. Acta A, 2021a, 250: 119223. DOI: 10.1016/j.saa.2020.119223.

Ogresta, L., Nekvapil, F., Tămaș, T., Barbu-Tudoran, L., Suciu, M., Hirian, R., Lazar, G., Levei, E., Glamuzina, B., Cîntă Pinzaru, S. Rapid and Application-Tailored Assessment Tool for Biogenic Powders from Crustacean Shell Waste: Fourier Transform-Infrared Spectroscopy Complemented with X-ray Diffraction, Scanning Electron Microscopy, and Nuclear Magnetic Resonance. ACS Omega 2021, 6: 27773-27780. DOI: 10.1021/acsomega.1c03279.

Rissouli, L., Beenicha, M., Chafik, T., Chabbi, M. Decontamination of water polluted with pesticide using biopolymers: Adsorption of glyphosate by chitin and chitosan. *J. Mater. Environ. Sci.* 2017, 8: 4544-4549.

Smith, B.C. Organic Nitrogen Compounds, Part I: Introduction. *Spectroscopy* 2019, 34: 10-15.

Smith, E., Dent, G. Modern Raman Spectroscopy – A Practical Approach. John Wiley & Sons, 2005, p. 15.

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EXECUTIVE SUMMARY

Project title:
New composites based on carotenoid-depleted seafood shell waste with efficient environmental pollutants adsorption

Project code:
PN-III-P1-1.1-PD-2021-0477

We consider a broader context of circular economy and the blue bioeconomy, where the shells, a common food waste, are viewed as a secondary raw material with potential applications. Thus, we target the production of adsorbent material from waste shells, but we also pay due consideration to the material preparation, its re-usability, and its handling after its useful (for adsorption) lifetime has run out.

Connecting the results obtained from SEM, FTIR and, acetone immersion causes the dissolution and removal of lipids located presumably inside the pores and crevices in shell structure. On the other hand, the rigid shell components, such as Mg-calcite biomineral and chitin scaffold remain largely unchanged. Consequently, the results indicate that the carotenoids extraction step from crustacean shells is beneficial to the current aim, as it allows obtaining, on one hand, valuable carotenoids (aim of another project) and, on the other hand, increased surface area of pores available for pollutant adsorption.

Investigations focused on chemical and thermal treatments with the aim of further increasing the pore surface area available for pesticides and antibiotics adsorption were done. Beyond that achieved by acetone extraction alone. These results will be made available through a patent application, a conference presentation, and a scientific article supported by the project funding.

Project director:
Dr. Fran Nekvapil