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# Review of the PhD Thesis

**of Ms. Sonia Żółtowska, entitled:**

**"**Extreme Biomimetics: Functionalization of renewable 3D biopolymer scaffolds and their application as catalysts"

Supervisor: Professor Teofil Jesionowski
Co-supervisor: Professor Hermann Ehrlich

## 1. Scope and significance of the thesis

One of the possible directions to solve the worldwide environmental crisis related to the pollution could be the increasing interest in "green-industry" and utilization of bio-wastes and biomass for producing the new generation of functional materials. Especially, bio-carbons with specific three-dimensional structures (scaffolds) obtained by transformation of the carbon-rich biomass (precursor) into a porous functional material has recently attracted particular attention with more that 2000 records in Scopus database in 2021.

Selection of precursor is critical for the final properties and morphology of the biomaterials. It is crucial to understand how the chemical and elemental composition of biomass influence the composition and structure of bio-carbon.

The most popular biomass which have been utilized to fabricate the bio-carbons are cellulose, various peels, fungal and crustacean chitin, egg white, lignin, spongin, collagen, and keratin. Huge diversity in the precursors and future application require selection the most suitable material and

development strategy for fabrication of bio-carbons with tailored structure and composition. Recently, the constant increase of interest in bio-carbons, their synthesis, functionalization, and applications for catalytic purposes is observed. The best precursor for such application should have a high carbon content and the presence of doping elements. Moreover, three-dimensional and nanoporous structure of the to enhance the catalytic properties are also required.
The unique properties of chitin and spongin make those biomaterials promising candidates to be precursors for novel bio-carbon advanced materials with a wide range of possible applications in pharmacy, cosmetic chemistry industry, or tissue engineering. For instance, composites of spongin and selected oxides have been successfully applied in energy storage devices or photocatalysts. Moreover, spongin-based scaffold after carbonization and further functionalization with of copper oxide(I) results in the formation of a three-dimensional catalyst with promising activity and enhanced mechanical properties.

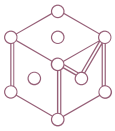
Taking into consideration the interesting features of both spongin and chitin, Ms. Sonia Żółtowska decided in her PhD work to apply them in extreme biomimetic approaches to prepare biologically inspired advanced composites for different catalysts. She studied and applied unique structure and physicochemical properties of spongin-based scaffolds particularly to produce bio-carbons functionalized and utilized further in development of new metal-based catalysts. Additionally, she aimed for developing novel sources of chitin, which do not require expensive structure formation.

To summarize, the scope of the thesis and proposed approaches are significantly relevant to current trends and challenges in the field of bio-carbons composites for catalytic applications.

## 2. Form and content

The basis of the reviewed doctoral dissertation is a thematically coherent collection of PhD student's 6 articles published on the recognized scientific journals. The collection of articles is preceded by a description of the most important research results obtained in the form of a several-dozen-page guide to these publications. It is a relatively new formula of doctoral theses chosen more and more often by PhD students who have decided to publish the results of their research before the defense.
All articles have been published as original multi-authored works in JCR-listed journals with high impact factors. The IF of these works ranges from 1.213 to 7.963, and the total IF is high and equal to 31.438. The PhD student is the first in all of them. She had a key share in the creation of all articles, expressed in the following percentages: 1 x 70%, 1 x 65%, 1 x 60% 1 x 55% and 2x 35%, which was confirmed by the declarations of the co-authors attached to the papers. The list of publications constituting the basis of the reviewed work is presented below:

1. Żółtowska-Aksamitowska S., Tsurkan M., Swee-Cheng L., Meissner H., Tabachnick K., Shaala L.A., Youssef D.T.A., Ivanenko V., Petrenko I., Wysokowski M., Bechman N., Joseph Y., Jesionowski T., Ehrlich H. (2018) The demosponge Pseudoceratina purpurea as a new source of fibrous chitin. International Journal of Biological Macromolecules 112: 1021–1028.



2. Żółtowska-Aksamitowska S., Shaala L.A., Youssef D.T.A., El Hady S., Tsurkan M., Petrenko I., Wysokowski M., Tabachnick K., Meissner H., Ivanenko V., Bechman N., Joseph Y., Jesionowski T., Ehrlich H. (2018) First report on chitin in non-verongiid marine demosponge: the Mycale euplectellioides case. Marine Drugs 16: 68
3. Żółtowska S., Koltsov I., Alejski K., Ehrlich H., Ciałkowski M., Jesionowski T. (2021) Thermal decomposition behaviour and numerical fitting for the pyrolysis kinetics of 3D spongin-based scaffolds. The classic approach. Polymer Testing 97: 107148
4. Żółtowska S., Modelska M., Piasecki A., Jesionowski T. (2020) Commercial sponges in heterogeneous catalysis: developing novel composites with cobalt and silver, Physicochemical Problems of Mineral Processing 56(6): 89–100.
5. Żółtowska S., Minambres J.F., Piasecki A., Mertens F., Jesionowski T. (2021) Threedimensional commercial-sponge-derived $Co_3O_4$@C catalysts for effective treatments of organic contaminants, Journal of Environmental Chemical Engineering 9(4): 105631
6. Żółtowska S., Bielan Z., Zembrzuska J., Siwińska-Ciesielczyk K., Piasecki A., Zielińska-Jurek A., Jesionowski T. (2021) Modification of structured bio-carbon derived from spongin-based scaffolds with nickel compounds to produce a functional catalyst for reduction and oxidation reactions: Potential for use in environmental protection. Science of the Total Environment 794: 148692

These publications have already been reviewed by representatives of the scientific community and are published in recognized and frequently cited journals in the disciplines of Chemical Sciences and Materials Science and Engineering. To sum up, the thematically coherent collection of 6 publications is a unique achievement of the PhD student, which deserves special emphasis and distinction in her scientific activity.

The main body of the dissertation is the publication guide, which is quite extensive and consists of 101 pages. It is written in English. It begins with a list of numerous scientific activities of the doctoral student, a list of publications constituting the basis of the doctoral dissertation and abstracts in English and Polish. The reader is introduced to the subject of the thesis by the next chapter - "Introduction". This chapters consists of 30 pages and provides a very good background for understanding the rest of the thesis. The main aspects of biomimetics in materials science are described in the historical order that they emerged. Special attention is given to spongin and chitin of marine sponge origin. The structure, chemical composition and properties of both natural polymers are discussed based on based on state-of-the-art literature review. The many possible applications of spongin and chitin in the field of materials science and engineering are presented, especially use of spongin or chitin as precursors of carbonized materials. The bio-carbons as metal phase support or structured catalysts are discussed in the next part of the introduction.
The introduction does not contain a summary of what research problem the PhD student wants to solve in the light of the current state of knowledge. There is also no clear formulation of the aims of the thesis. A research hypothesis is not stated too. Although it is not required in doctoral dissertations, its statement requires the candidate to thoroughly analyze the scientific problem and propose an approach to its solution.

The main part of the dissertation is the description of the content of the 6 publications constituting the basis of the thesis.

First two publications (**1** and **2**) are about new sources of chitin. For the first time, the presence of chitin in species P. purpurea and M. euplectellioides was investigated. The chitin was isolated using a sodium hydroxide based demineralization, followed by decalcification, deproteinization and desilicification. The obtained materials were characterized using calcofluor white staining, FTIR analysis, electrospray ionization mass spectrometry (ESI-MS), scanning electron microscopy (SEM), fluorescence microscopy, and chitinase digestion test. The presence of alpha-chitin in the skeleton of both sponges was confirmed.

Spongin-based scaffold as a as a source of bio-carbons was described in detail in the publication **3**. 3D biopolymer structures were isolated from Hippospongia communis marine demosponge, and then their thermal degradation was characterized by using thermogravimetric analysis. Two-weight losses were observed at temperatures 80-150 °C and at temperatures 200-420 °C, which is related to evaporation of the absorbed water and the decomposition of peptide bonds, respectively. Additionally, the release of various gases such as $H_2O$, $CO_2$, $NH_3$, $NO_x$, HCN, $SO_2$, $H_2S$, hydrocarbons during heating were recognized using mass spectrometry. The most important achievement of this publication was modelling the kinetics of spongin pyrolysis.

In publication **4**, functionalization of the spongin-scaffold was performed by immobilization of cobalt and silver cations, followed by reduction reaction using sodium borohydride. The resulted composite materials were studied. The catalytic properties of the composites in the reaction of reduction of 4-nitrophenol to 4-aminophenol in water were confirmed.

The carbonized spongin based scaffolds functionalized with cobalt oxide are described in publication **5**. The prepared materials were tested as potential catalysts in the oxidation of styrene, decolorization of rhodamine B, and reduction of 4-nitrophenol. High catalytic activity and reusability in both oxidation and reduction reactions were achieved.

Bio-carbons from spongin-based scaffolds modified with nickel hydroxide, oxide, and metallic nickel to produce a functional catalyst for reduction and oxidation reactions was the topic of the last publication (**6**). After modification, scaffold surface consisted of up to 26.0 wt% of the nickel-based phases, and various heteroatoms, including nitrogen, sulfur, oxygen, iron, silica, and aluminum. The all materials possess similar activity in reduction of 4-nitrophenol. The catalytic oxidation reactions were proved at different pH using phenol, methylchlorophenoxypropionic acid (MCPP), and 4-chlorophenoxyacetic acid (4 CPA) as substrates.

The summary of the PhD work is presented in the Chapter **7**. The main scientific achievements and overall conclusions are listed in this part of the dissertation. In the Chapter **8**, the Author defines unsolved issues and proposes future research directions. The last chapter is bibliography consisting of 229 scientific articles, closely related to the topic of the thesis.

The overall quality of the dissertation is excellent. It is clearly structured and easy to read. The style and English language are satisfactory. The Author comprehensively presented findings using several tables (6) and figures (21). There are some editorial errors, but it doesn't detract from the value of the content. For instance, Fig. 12. c and d are not described figure caption, and supplementary material for publication **2** is missing. In summary, the thesis is very well prepared.

## 3. Scientific content and substantive aspects

Ms. Sonia Żółtowska has submitted a thesis that significantly exceeds typical requirements for the doctoral dissertations. After an extensive analysis of current state-of-the art in the field of bio-carbons porous scaffolds obtained from the biomass, she performed well-organized and high-quality research to investigate:

- new sources of chitin in sponges of Demosponginae class;
- spongin-based scaffolds pyrolysis and fabrication the advanced composites with catalytic properties.

The topic of the thesis of Ms. Sonia Żółtowska is very relevant, meaningful, and actual. Doctoral candidate has revised the relevant literature and acquired knowledge and understanding of the thesis related topics. Nowadays, there is a growing demand for developing new bio-carbon based scaffolds with catalytic properties. The thesis demonstrates an original work which makes an important contribution to knowledge in the field of extreme biomimetics. It is related to the field of novel advanced materials for catalysts. A strength of the work are novel approaches in isolation, carbonization and functionalization of biomaterials used to develop highly porous 3D structure with interesting catalytic properties. It contains original results and promising insights in the field of chitin and spongin-based precursors for bio-carbons.
For the first time, the chitin was isolated from species P. purpurea and M. euplectellioides. The isolated chitin resembles the shape of a sponge skeleton and is built from α-chitin polymorph. The FTiR spectra confirms the purity of isolated chitinous scaffolds.
Another significant achievement of the PhD work is extensive investigation of the kinetics of thermal degradation of spongin-based scaffolds using thermogravimetric analysis (TGA) and various mathematical models. The TGA revealed that the thermal degradation of the spongin does not depend on the heating regime. The chemical reaction model properly described the kinetics of pyrolysis.
The unique low-temperature pyrolysis and functionalization of spongin-based scaffolds with cobalt, silver and nickel and application in various oxidation-reduction reactions are the most important results of the thesis. The effectiveness of pyrolysis and functionalization was properly evaluated using various techniques, including Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDS), TEM, thermogravimetric analysis (TGA), XPS and BET and Raman spectroscopy.

When reading a PhD thesis, the following questions arise:

1. Can you summarize the metal-based catalysts advantages and disadvantages?
2. How different were the geometries/mass of the spongin-based scaffolds in each of the papers?
3. What were the metallic phases content and crystallinity in different spongin-based scaffolds? Was the coating homogeneous? Was the durability/stability of the coating evaluated? How could the coating properties influence their catalytic properties?
4. Why were the mechanical properties of the developed advanced composite materials not evaluated? They could be important considering future applications of the developing

materials. How do the thermal treatment and chemical functionalization could influence the mechanical properties?

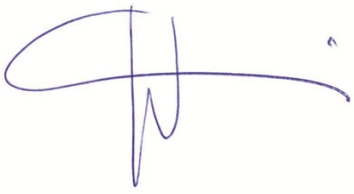
5. How to improve efficiency and selectivity of the spongin-based catalysts with cobalt and nickel phases? Could you compare the catalytic performance of the developed catalysis and metal sponges?

In summary, the reviewed doctoral dissertation has many cognitive aspects and is an original contribution to the development of the field of biological materials and their various applications. The greatest achievements of the dissertation are the discovery of new sources of chitin and the use of a sponge for the first time to obtain advanced composite materials with impressive catalytic properties.

## 4. Final conclusions

Considering the groundbreaking results obtained by Ms. Sonia Żółtowska, good mastery of the research technique and correct interpretation of the research results, herein it can be concluded that her doctoral dissertation meets all conditions specified in Article 187 of Act of July 20, 2019 Law on Higher Education and Science (Journal of Lawa of 2018, item 1668, as amended), and thus I am asking the Scientific Council of Chemical Sciences of Poznan University of Technology for admission Ms. Sonia Żółtowska to the next stages of the doctoral process.
At the same time, due to the high quality and importance of the results of the dissertation, outstanding scientific achievements that have been published in several leading scientific journals, the reviewed work deserves a distinction.

Sincerely yours,



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