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REVIEW

of PhD dissertation by Sonia Żółtowska, MSc, Eng entitled "*Extreme Biomimetics: Functionalization of renewable 3D biopolymer scaffolds and their application as catalysts*" made in the Institute of Chemical Technology and Engineering at the Faculty of Chemical Technology of the Poznan University of Technology. Professor Teofil Jesionowski is the supervisor of the doctoral dissertation and Professor Hermann Ehrlich is co-supervisor.

Choice of topic and relevant research areas

PhD dissertation by Sonia Żółtowska, MSc, Eng is devoted to the studies of marine sponges and is located in the context of contemporary research about material science and biomimetics.

In science, new ideas very often arise in the emergence of a careful study of nature and then their transfer to technology and relevant applications. For example, biopolymers can be successfully used to obtain carbon materials. Among a wide range of biopolymers commonly used in the preparation of bio-carbons, spongin-based scaffolds are a very promising choice. Spongin is considered an interesting material due to its thermal stability, fibrous-like structure, three-dimensional morphology, and the presence of various heteroatoms in the structure. It also seems to have the potential to be used in preparation of advanced supports for catalysis purposes. Additionally, their use is economically feasible, because they are cultivated on a large scale under marine farming conditions.

The reviewed dissertation is thematically coherent. It concerns important and current topics related to the study of evaluation of new sources of chitin in sponges (specifically Demosponginae class) and applying spongin-based

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scaffolds isolated from commercial sponges to obtain novel hybrid materials based on carbonized spongin scaffolds or spongin itself.

The results of such research are very important because they may provide a significant insight into the development of efficient and new bioinspired materials. The issues discussed in the dissertation are the scientific domain of the groups of Professor Teofil Jesionowski and Professor Hermann Ehrlich.

Structure of dissertation

The reviewed PhD thesis of Sonia Żółtowska is based on the coherent collection of 6 scientific articles published in international journals:

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, IF= 6.953, output 35%;

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, IF= 5.118, output 35%;

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, IF= 4.282, output 55%;

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, IF= 1.213, output 70%;

5 Żółtowska S., Minambres J.F., Piasecki A., Mertens F., Jesionowski T. (2021) ***Three - dimensional commercial-sponge-derived Co_3O_4@C catalysts for effective treatments of organic contaminants***. Journal of Environmental Chemical Engineering, 9(4): 105631, IF= 5.909, output 65%;

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, IF= 7.963, output 60%.

The total Impact Factor of the publication is very high and equal to IF_{2020}= 31.438, which gives the average value per publication IF = 5.239.

The PhD student is the first author in all publications, her individual output is in the range of 35-70%, which indicates that her participation in the development of the research plan, its implementation, conducting studies, interpretation of the results and preparation of the above-mentioned articles was significant. All publications included in the dissertation are characterized by a very good scientific level and care for appropriate presentation, documentation and discussion of the presented results and conclusions. They were reviewed by a group of selected experts, so their high scientific level was confirmed.

The PhD dissertation has 229 pages and is written in English. It consists of a list of scientific activity of PhD Student, an abstract in English and Polish, an introduction, a description of the content of publications, summary, future outlook, a bibliography (229 items) and attachments in the form of reprints of articles chosen as the basis for PhD procedure, as well as statements of co-authors of these publications. The Author has a very good command of relevant literature on this topic, as confirmed by the extensive review presented in Chapter 5.

The research presented in the doctoral dissertation was carried out, among others, under the grant: The National Science Center (Poland), Etiuda 7 Grant no. 2019/32 / T / ST8 / 00414, *Extreme Biomimetics: Functionalization of renewable 3D biopolymer scaffolds and their application as catalysts*, (7.10.2019-6.04 .2020).

Substantive assessment

The scope of the doctoral thesis is mainly focused on two aims: 1) investigation of new sponge species having the skeleton made of chitin within Demosponginae sponge class and 2) evaluation of the spongin-based scaffolds pyrolysis and investigation of their usefulness to produce the advanced composites based on spongin or on biocarbons received after carbonization.

In the dissertation new sources of chitin were discovered and described, presenting a detailed study of the isolation and identification of chitin from the skeleton (**publications 1 and 2**). Obtained results showed that chitin preserved the structure of the sponge skeleton and might be applied as ready-to-use scaffolds for various applications. It was the first attempt to extract and identify α-chitin from *Pseudoceratina purpurea* (from coastal waters of Singapore) (pub. 1) and from *Mycale euplectellioides* (from Red Sea) (pub. 2). The identification of chitin was carried out using various bioanalytical tools such as e.g. Calcofluor white staining, Fourier-

transform infrared spectroscopy (FTIR), electrospray ionization mass spectrometry (ESI-MS, fluorescence microscopy, a chitinase digestion assay.

In **publication 3** for the first time, the thermal decomposition behavior of spongin-based scaffolds isolated from *Hippospongia communis* marine demosponge was characterized by thermogravimetric analysis. Additionally, the study of volatile products released during the thermal treatment was performed using mass spectrometry.

The functionalization of spongin-based scaffolds with cobalt and silver by immobilization of particular ions followed by reduction with sodium borohydride was described in **publication 4**. The characterization of obtained composite materials and their application as heterogeneous catalysts in the reduction reaction of 4-nitrophenol to 4-aminophenol in water were presented.

Publication 5 is concerned with the resulted biocarbons, which were modified with cobalt to obtain the materials mainly covered by cobalt oxide Co_3O_4. The carbonization was carried out at temperatures of 400°C, 500°C, and 600°C. The main focus was on utilization of prepared materials as potential catalysts in the reactions of oxidation of styrene, decolorization of rhodamine B with hydrogen peroxide, and reduction of 4-nitrophenol with sodium borohydride. The oxidation of styrene was carried out using two oxidants: hydrogen peroxide and tert-butyl hydroperoxide. The progress of each reaction was monitored by UV-Vis spectroscopy. Based on the literature, the mechanism of styrene oxidation was proposed.

In **publication 6** a spongin-based fibrous scaffold (isolated from the marine demosponge Hippospongia communis) was utilized as a precursor of a carbon support, subjected to carbonization (at 400, 500, 600°C) and then modification with nickel and nickel oxide. The highest efficiency of nickel functionalization was achieved for the NiO/Ni(OH)2/Ni_600 catalyst (26.01% mass of Ni), and the lowest for the sample carbonized at 500°C (15.19% mass of Ni). The results showed that the temperature of carbonization influences the effectiveness of the modification process and confirmed the promising activity of obtained materials in the reduction of 4-nitrophenol to 4-aminophenol. The mechanism of the reduction process was also proposed. The compounds commonly used in the production of drugs (phenol) and pesticides (methylchlorophenoxypropionic acid (MCPP) and 4-chlorophenoxyacetic acid (4-CPA)) were used as substrates for the catalytic oxidation reaction. NiO/Ni(OH)2/Ni_400 catalyst showed excellent catalytic ability in the oxidation of MCPP and 4-CPA (99% oxidation efficiency at pH 3) and good activity in the oxidation of phenol (80% yield at pH 3). Additionally, the use of hydrogen peroxide as an oxidizing agent made it possible to eliminate the formation of additional toxic products of oxidant decomposition. High level of catalytic activity was related to the multiphase composition of the nickel-containing phase, a variety of active centers of catalyst

and the evenly distributed metal-containing phase, which acts synergistically with the three-dimensional structure of support, enhancing the diffusion of reagents to the catalyst's surface.

Taking into account the obtained results and the discussion as the most valuable in the presented work, I would like to highlight:

1. Statement for the first time that chitin is present as a structural component in skeletons of the Verongiida sponge *P. purpurea* and non-verongiid representative of Mycale genus Red Sea demosponge *M. euplectelloides*. It resembles the shape of a sponge skeleton and is built from α-chitin polymorph.
2. Conducting the investigation of spongin-based scaffolds proving its potential and usefulness as a source for producing the biocarbons by calculating the kinetics of its thermal degradation using thermogravimetric analysis.
3. Statement that the temperature of carbonization directly impacts the final structure and chemical composition of the material.
4. Successful utilization of a spongin-based scaffold for a cobalt oxide-based catalyst applied in oxidation-reduction reactions without a significant loss of activity in several cycles. Proving with the use of the kinetic and reusability studies that the functionalization with metallic particles led to obtaining materials with great catalytic performance, good reusability properties, and significantly higher thermal stability.
5. Development for the first time of a relatively simple method of functionalization of carbonized scaffolds to obtain nickel-based bio-carbon composites.
6. Proposition of the mechanisms of styrene oxidation and reduction of 4-nitrophenol to 4-aminophenol.
7. Carrying out research focused on in-depth analysis of morphological and physicochemical characterization of obtained nickel-based materials and their testing as a potential catalyst of oxidation and reduction of various emerging phenolic compounds.
8. Applying a wide range of techniques e.g. XPS, XRD, XRF, SEM-EDS, TEM, FTIR, low-temperature N_2 sorption isotherms, UV-Vis spectroscopy to characterize physicochemical and morphological properties of studied materials.
9. Good adequacy of the research approach and methodology for the given problems.
10. Excellent quality of the conclusions in the context of the original problem statement, and the evidence that is presented.
11. The work concerns a highly current subject, both in terms of cognitive and practical, and brings elements of novelty in the scope of the discussed subject.

The specific questions/remarks addressed to the doctoral dissertation are given below. I expect the candidate refer to them during the public defense:

1. What is the opinion of the PhD student about the repeatability of the natural materials used in the work and, as a consequence, of their properties?
2. What is the opinion of the PhD student about undertaking more detailed studies of elemental composition of applied sponge that may depend on the environment and could be incorporated into the skeletons during the sponge's growth in natural water? What other techniques could be used?
3. How can the difference in the BET surface area for cobalt and nickel catalysts of prepared materials be explained? -"The highest value was measured for Co_3O_4@C500 equaled 26.3 m^2/g. Then, the values gradually decreased to be 6.4 and 5.1 m^2/g for Co_3O_4@C400 and Co_3O4@C600, respectively". In the case of nickel catalysts - "the low value of BET surface area, which does not exceed 10 m^2/g".
4. In what other reactions could the obtained catalytic systems be applied?

SUMMARY

In the assessment of the work, I conclude that it concerns important and current topics in the area of the production, characterization, and practical application of materials based on spongin and chitin. The method of planning the research, its execution, the form of presenting the results and their analysis prove the high scientific and research maturity of the Author of the dissertation.

The PhD student has significant publishing achievements. She is a co-author of 26 articles published in journals from the JCR list (including 6 articles related to the dissertation), 2 chapters and 17 (9 oral and 8 poster) conference presentations of national and international scope, which proves the Author's high activity in disseminating the issues of the doctoral dissertation and other scientific achievements in the scientific community.

I am convinced that the reviewed PhD dissertation by Sonia Żółtowska, MSc, Eng entitled "Extreme Biomimetics: Functionalization of renewable 3D biopolymer scaffolds and their application as catalysts" made in the Institute of Chemical Technology and Engineering at the Faculty of Chemical Technology of the Poznan University of Technology meets the requirements for doctoral theses (Articles 16 and 17 of the Act of March 14, 2003 on academic degrees and the academic title as well as degrees and title in the field of art - as amended) and I request the Discipline Council of Chemical Sciences to admit the PhD student to further stages of the doctoral dissertation.

Taking into account the scope, level and importance of the research and a very high scientific activity of the PhD student, I apply for the distinction of the reviewed doctoral dissertation because:

1. It shows a very good quality of the PhD thesis confirmed by 6 publications in highly recognized research journals (IF from 1.213 to 7.963; average value per publication IF = 5.239).
2. It introduces elements of novelty in the scope of the discussed subject.
3. It contains extensive and original experimental material based on reliable results obtained with the use of many analytical techniques.
4. The obtained results are of practical importance and contribute to the progress in the preparation and application of bio-inspired materials, which is in line with the principles of green chemistry and sustainable development.
6. The PhD student has very good academic achievements and is a co-author of 26 articles.

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