Poznan University of Technology

Faculty of Chemical Technology

Institute of Chemical Technology and Engineering

PhD thesis

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

Sonia Żółtowska, M. Sc., Eng.

Supervisor: Professor Teofil Jesionowski

Co-supervisor: Professor Hermann Ehrlich

Poznań, 2021

ACKNOWLEDGEMENTS

I would like to impress my gratitude to many people involved in the various stages of development of this doctoral thesis.

First of all, I would like to thank my supervisor, **Professor Teofil Jesionowski,** for his scientific support, advice, and discussions, and the opportunity to study under his supervision.

I would like to thank Professor Michał Ciałkowski for his great support and help in understanding the kinetics aspects of thermal degradation.

I would like to express my gratitude for all my co-authors, colleagues, and students from the Faculty of Chemical Technology, especially:
Adam Kubiak
Filip Ciesielczyk
Katarzyna Siwińska-Ciesielczyk
Krzysztof Alejski

I would like to acknowledge my co-supervisor, **Professor Hermann Ehrlich,** and his team members, as well as
Professor Florian Mertens and Professor Monika Mazik, for all their help during my stay at TU Bergakademie Freiberg.

I would like to thank my co-workers from the Faculty of Forestry and Wood Science of the University of Life Sciences in Prague for their support in the last stage of preparation of this thesis.

Last but not least, I would like to thank my **Family and Friends** who have always been with me and supported me throughout my life, during the PhD studies and preparation of this thesis.

Franiu, Mamo, Babciu, Tato, Weroniko, Danielu, Kryśku, Michale, Mateuszu – DZIĘKUJĘ

“Happiness can be found, even in the darkest of times,
if one only remembers to turn on the light”

— J.K. Rowling

“Trzeba mieć wytrwałość i wiarę w siebie.
Trzeba wierzyć, że człowiek jest do czegoś zdolny
i osiągnąć to za wszelką cenę”

— Maria Skłodowska-Curie

For my Husband and our *Little one*

TABLE OF CONTENTS

1. SCIENTIFIC ACTIVITY

- PEER-REVIEWED PAPERS

1) Kubiak A., **Żółtowska S**., Borowiak, A., Gabała E., Sacharczuk N., Zalas M., Siwińska-Ciesielczyk K., Jesionowski T. (2021) The TiO_2-ZnO systems with multifunctional applications in photoactive processes – efficient photocatalyst under UV-LED light and electrodes materials in DSSCs, *Materials* 14(20): 6063 (IF 3.623).
2) **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).
3) **Żółtowska S**., Miñambres 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).
4) Kubiak A., **Żółtowska, S.,** Gabała E., Szybowicz M., Siwińska-Ciesielczyk K., Jesionowski T. (2021) Controlled microwave-assisted and pH-affected growth of ZnO structures and their photocatalytic performance, *Powder Technology* 386: 221-235 (IF 5.134).
5) **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).
6) **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).
7) Machałowski T., Wysokowski M., Tsurkan M.V., Galli, R., Schimpf C., Rafaja D., Brendler E., Viehweger C., **Żółtowska-Aksamitowska S.,** Petrenko I., Czaczyk K., Kraft M., Bertau M., Bechmann N., Guan K., Bornstein S.R., Voronkina A., Fursov A., Bejger M., Biniek-Antosiak K., Rypniewski W., Figlerowicz M., Pokrovsky O., Jesionowski T., Ehrlich H. (2019) Spider Chitin: An ultrafast microwave-assisted method for chitin isolation from *Caribena versicolor* spider molt cuticle, *Molecules* 24(20): 3736 (IF 4.411).
8) Machałowski T., Wysokowski M., **Żółtowska-Aksamitowska S.,** Bechmann N., Binnewerg B., Schubert M., Guan K., Bornstein S.R., Czaczyk K., Pokrovsky O., Kraft M., Bertau M., Schimpf C., Rafaja D., Tsurkan M., Galli R., Meissner H., Petrenko I., Fursov A., Voronkina A., Figlerowicz M., Joseph Y., Jesionowski T., Ehrlich H. (2019) Spider Chitin. The biomimetic potential and applications of *Caribena versicolor* tubular chitin, *Carbohydrate Polymers* 226(15): 115301 (IF 9.381).
9) Petrenko I., Summers A.P., Simon P., **Żółtowska-Aksamitowska S.,** Motylenko M., Schimpf C., Rafaja D., Roth F., Kummer K., Brendler E., Pokrovsky O.S., Galli R., Wysokowski M., Meissner H., Niederschlag E., Joseph Y., Molodtsov S.,

Ereskovsky A., Sivkov V., Nekipelov S., Petrova O., Volkova O., Bertau M., Kraft M., Rogalev A., Kopani M., Jesioniowski T., Ehrlich H. (2019) Extreme Biomimetics: Preservation of molecular detail in centimeter scale samples of biological meshes laid down by sponges, *Science Advances* 5(10): eaax2805 (IF 14.136).

10) Jesionowski T., Jankowska K., Jędrzak A., Szalaty T.J., **Żółtowska-Aksamitowska S.,** Klapiszewski Ł., Kołodziejczak-Radzimska A., Stasiewicz M., Wysokowski M., Zdarta J. (2018) Zaawansowane funkcjonalne materiały wytwarzane z użyciem substancji pochodzenia naturalnego, *Przemysł Chemiczny* 97(12): 2026–2036 (IF 0.464).

11) Klinger C., **Żółtowska-Aksamitowska S.,** Wysokowski M., Tsurkan M.V., Galli R., Petrenko I., Machałowski T., Ereskovsky A., Martinović R., Muzychka L., Smolii O.B., Bechmann N., Ivanenko V., Schupp P.J., Jesionowski T., Giovine M., Joseph Y., Bornstein S.R., Voronkina A., Ehrlich H. (2019) Express method for isolation of ready-to-use 3D chitin scaffolds from *Aplysina archeri* (Aplysineidae: Verongiida) Demosponge, *Marine Drugs* 17(2): 131 (IF 5.118).

12) Shaala L.A., Asfour H.Z., Youssef D.T.A., **Żółtowska-Aksamitowska S.,** Wysokowski M., Tsurkan M., Galli R., Meissner H., Petrenko I., Tabachnick K., Ivanenko V.N., Bechmann N., Muzychka L.V., Smolii O.B., Martinovic R., Joseph Y., Jesionowski T., Ehrlich H. (2019) New source of 3D chitin scaffolds: the Red Sea Demosponge *Pseudoceratina arabica* (Pseudoceratinidae, Verongiida), *Marine Drugs* 17(2): 92 (IF 5.118).

13) Fromont J., **Żółtowska-Aksamitowska S.,** Galli R., Meissner H., Erpenbeck D., Vavelet J., Diaz C., Tsurkan M.V., Petrenko I., Youssef D.T.A., Ehrlich H. (2019) New family and genus of a Dendrilla-like sponge with characters of Verongiida. Part II. Discovery of chitin in the skeleton of *Ernstilla lacunose, Zoologischer Anzeiger* 280: 21–29 (IF 1.521).

14) Ciesielczyk F., **Żółtowska-Aksamitowska S.,** Jankowska K., Zembrzuska J., Zdarta J., Jesionowski T. (2019) The role of novel lignosulfonate-based sorbent in a sorption mechanism of active pharmaceutical ingredient: batch adsorption tests and interaction study, *Adsorption* 25(4): 865–880 (IF 2.318).

15) Ghanbari M.H., Shahdost-Fard F., Khoshroo A., Rahimi-Nasrabadi M., Ganjali M.R., Wysokowski M., Rębiś T., **Żółtowska-Aksamitowska S.,** Jesionowski T., Rahimi P., Joseph Y., Ehrlich H. (2019) A nanocomposite consisting of reduced graphene oxide and electropolymerized β-cyclodextrin for voltammetric sensing of levofloxacin, *Microchimica Acta* 186: 438 (IF 5.833).

16) Klinger C., **Żółtowska-Aksamitowska S.,** Jesionowski T. (2019) Isolation of chitin from *Aplysina aerophoba* using a microwave approach, *Progress on Chemistry and Application of Chitin and its Derivatives* 24: 61-67 (IF 0.630).

17) **Żółtowska-Aksamitowska S.,** Bartczak P., Zembrzuska J., Jesionowski T. (2018) Removal of hazardous non-steroidal anti-inflammatory drugs from aqueous solutions by biosorbent based on chitin and lignin, *Science of the Total Environment* 612: 1223–1233 (IF 7.963).

18) Szatkowski T., Kopczyński K., Motylenko M., Borrmann H., Mania B., Graś M., Lota G., Bazhenov V.V., Rafaja D., Roth F., Weise J., Langer E., Wysokowski M., **Żółtowska-Aksamitowska S.,** Petrenko I., Molodtsov S.L., Hubálková J.,

Aneziris C.G., Joseph Y., Stelling A.L., Ehrlich H., Jesionowski T. (2018) Extreme biomimetics: carbonized 3D spongin scaffold as a novel support for nanostructured manganese oxide (IV) and its electrochemical applications, *Nano Research* 11(8): 4199–4214 (IF 8.183).

19) Norman M., **Żółtowska-Aksamitowska S.,** Zgoła-Grześkowiak A., Ehrlich H., Jesionowski T. (2018) Iron(III) phthalocyanine supported on a spongin scaffold as an advanced photocatalyst in a highly efficient removal process of halophenols and bisphenol A, *Journal of Hazardous Materials* 347: 78–88 (IF 8.897).
20) **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).
21) **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).
22) Ehrlich H., Wysokowski M., **Żółtowska-Aksamitowska S.,** Petrenko I., Jesionowski T. (2018) Collagens of poriferan origin, *Marine Drugs* 16: 79 (IF 5.118).
23) Jesionowski T., Norman M., **Żółtowska-Aksamitowska S.,** Petrenko I., Yoseph Y., Ehrlich H. (2018) Marine spongin: naturally prefabricated 3D scaffold-based biomaterial, *Marine Drugs* 16: 88 (IF 5.118).
24) Ehrlich H., Shaala L.A., Youssef D.T.A, **Żółtowska-Aksamitowska S.,** Tsurkan M., Galli R., Meissner H., Wysokowski M., Petrenko I., Tabachnik K., Ivanenko V.N., Bechmann N., Joseph Y., Jesionowski T. (2018) Discovery of chitin in skeletons of non-verongiid Red Sea demosponges, *PLOS one* 13(5): e0195803 (IF 3.240).
25) Wysokowski M., Bartczak P., **Żółtowska-Aksamitowska S.,** Chudzińska A., Piasecki A., Langer E., Bazhenov V.V., Petrenko I., Noga T., Stelling A.L., Ehrlich H., Jesionowski T. (2017) Adhesive stalks of diatom *Didymosphenia geminata* as a novel biological adsorbent for hazardous metals removal, *CLEAN - Soil, Air, Water* 45(11): 1600678 (IF 1.770).
26) Bartczak P., **Żółtowska S.,** Norman M., Klapiszewski Ł., Zdarta J., Komosa A., Kitowski I., Ciesielczyk F., Jesionowski T. (2015) Saw-sedge *Cladium mariscus* as a functional low-cost adsorbent for effective removal of 2,4-dichlorophenoxyacetic acid from aqueous systems, *Adsorption* 22: 517–529 (IF 2.318).

- BOOKS AND BOOKS CHAPTERS

1) Bartczak P., **Żółtowska S.,** Jesionowski T. (2016) Zanieczyszczenia układów wodnych związkami organicznymi – aktualne problemy i rozwiązania. In: G. Schroeder, P. Grzesiak (Eds.), Środowisko i przemysł, tom 6, Cursiva, ISBN 978-83-62108-35-0, (*in Polish*).

2) **Żółtowska-Aksamitowska S.,** Klinger Ch., Petrenko I., Wysokowski M., Joseph Y., Jesionowski T., Ehrlich H. (2019) Methods of Isolating Chitin from Sponges (Porifera), In: L.A.M. van den Broek, C. Boeriu (Eds.), Chitin and Chitosan: Properties and Applications, Wiley, Online ISBN:9781119450467; DOI:10.1002/9781119450467.

- CONFERENCES & SYMPOSIA
- Oral presentations

1) **Żółtowska-Aksamitowska S.,** Petrenko I., Wysokowski M., Joseph I., Jesionowski T. Marine Biomaterials: development of new carbonized 3D spongin based catalyst, *5th EuroBioMat*, 8-9.05-2019, Weimar, Germany.
2) **Żółtowska-Aksamitowska S.,** Petrenko I., Wysokowski M., Joseph I., Jesionowski T. Extreme Biomimetics: functionalization of nanostructured 3D carbon-spongin-composites, *World Congress on Functional Materials and Nanotechnology*, 14-15.05.2019, Valencia, Spain.
3) Ciesielczyk F., **Żółtowska-Aksamitowska S.,** Szczekocka W., Zembrzuska J., Klapiszewski Ł., Jesionowski T. The development of hybrid lignosulfonate-based materials for adsorption of active pharmaceutical ingredients, *Tenth International Symposium „Effects of Surface Heterogeneity in Adsorption, Catalysis and related Phenomena*“, 27-31.08.2018, Lublin, Poland.
4) **Żółtowska-Aksamitowska S.,** Petrenko I., Wysokowski M., Jesionowski T., Ehrlich H. Functionalization of 3D carbonized spongin scaffolds with respect to selected metal oxides, „*NanoBioMateriały – teoria i praktyka*”, 06-08.06.2018, Torun, Poland.
5) **Żółtowska-Aksamitowska S.,** Jesionowski T. Biomimetic, three-dimensional carbonaceous materials as a support for selected metal particles, *Baltic University Programme, V PhD Students Training,* Interdisciplinary-Multicultural-International, 27.11-01.12.2017, Rogów, Poland.
6) **Żółtowska-Aksamitowska S.,** Łukaszewska N., Wysokowski M., Ehrlich H., Jesionowski T. Three-dimensional carbonaceous materials as a support for deposition of selected metal particles, *XIIth Summer School for PhD Students and Young Researchers*, 25-30.06.2017, Sudomie, Poland.
7) **Żółtowska-Aksamitowska S.,** Krawczyk P., Gralewicz P., Wysokowski M., Ehrlich H., Jesionowski T. Aspekty fizykochemiczne i kinetyczne karbonizacji szkieletu gąbki morskiej z gatunku *Hippospongia communis*, *Konferencja „NanoBioMateriały – Teoria i Praktyka*”, 29-31.05.2017, Toruń, Poland.
8) **Żółtowska-Aksamitowska S.,** Wysokowski M., Ehrlich H., Jesionowski T. Biomimetyczne, trójwymiarowe struktury węglowe, *XV Seminatium Doktorantów „Na Pograniczu Chemii i Biologii*”, 21-24.05.2017, Karpacz, Poland.

9) **Żółtowska-Aksamitowska S.,** Bartczak P., Zembrzuska J., Jesionowski T. Wysokosprawna chromatografia cieczowa w ocenie efektywności adsorpcji wybranych farmaceutyków z układów wodnych, *Monitoring and water analysis. Chromatographic methods for the determination of ionic compounds,* 2-4.04.2017, Toruń, Poland.

- Poster presentation

10) **Żółtowska-Aksamitowska S.,** Klinger Ch., Petrenko I., Machałowski T., Wysokowski M., Jesionowski T., Ehrlich H. Sponges (porifera) as source of morphologically defined chitin, Konferencja Polskiego Towarzystwa Chitynowego: „*Nowe aspekty w chemii i zastosowaniu chityny i jej pochodnych*", 19-21.09.2018, Tyniec, Poland.

11) Petrenko I., Volkova O., Wysokowski M., **Żółtowska-Aksamitowska S.,** Jesionowski T., Ehrlich H. Extreme Biomimetics: steel melting process on 3D carbonized spongin scaffold, „*NanoBioMateriały – teoria i praktyka*", 06-08.06.2018, Toruń, Poland.

12) **Żółtowska-Aksamitowska S.,** Łukaszewska N., Ehrlich H., Jesionowski T. Spongina jako naturalny nośnik cząstek metali do zastosowań katalitycznych, BioOrg 2017, *II Ogólnopolskie Seminarium Chemii Bioorganicznej, Organicznej i Biomateriałów,* 2.12.2017, Poznań, Poland.

13) **Żółtowska-Aksamitowska S.,** Bartczak P., Zembrzuska J., Jesionowski T. Adsorpcja jako skuteczna metoda usuwania farmaceutyków z układów wodnych aspekt kinetyczny i termodynamiczny, *Monitoring and water analysis. Chromatographic methods for the determination of ionic compounds,* 2-4.04.2017, Toruń, Poland.

14) **Żółtowska S.,** Bartczak P., Jesionowski T. Termodynamiczne i kinetyczne aspekty usuwania pestycydu z modelowych roztworów wodnych z wykorzystaniem materiału pochodzenia roślinnego, *I Wielkopolskie Seminarium Chemii Bioorganicznej, Organicznej i Biomateriałów*, 5.12.2015, Poznań, Poland.

15) Bartczak P., **Żółtowska S.,** Zdarta J., Ciesielczyk F., Komosa A., Kitowski I., Jesionowski T. Usuwanie kwasu 2,4-dichlorofenoksyoctowego (2,4-D) z układów wodnych z wykorzystaniem adsorbentu pochodzenia roślinnego, *Nauka i Przemysł, Metody Spektroskopowe w Praktyce, Nowe Wyzwania i Możliwości*, 9-12.06.2015, Lublin, Poland.

16) Bartczak P., **Żółtowska S.,** Ciesielczyk F., Zdarta J., Jesionowski T. Usuwanie kwasu 2,4-dichlorofenoksyoctowego (2,4-D) z układów wodnych z wykorzystaniem adsorbentu pochodzenia roślinnego, *Konferencja Młodych Naukowców VII*, 17.01.2015, Wrocław, Poland.

17) Bartczak P., **Żółtowska S.,** Zdarta J., Ciesielczyk F., Jesionowski T. Kinetyka procesu adsorpcji kwasu 2,4-dichlorofenoksyoctowego (2,4-D) z układów

wodnych, *Chemia – Nowe Wyzwania dla Nauki i Przemysłu*, 5.12.2014, Poznań, Poland.

- Obtained research grants

1) German Academic Exchange Service, Short Term Research Grant, Project title: Extreme Biomimetics: Carbonization and metallization of *Hippospongia communis* marine sponge skeleton for development of an effective catalyst, 1.07.2017-30.11.2017.
2) The National Science Centre (Poland), Etiuda 7 Grant no. 2019/32/T/ST8/00414, Project title: Ekstremalna Biomimetyka: funkcjonalizacja odnawialnych, trójwymiarowych matryc biopolimerowych oraz ich zastosowanie jako katalizatorów (Extreme Biomimetics: Functionalization of renewable 3D biopolymer scaffolds and their application as catalysts), 7.10.2019-6.04.2020.

2. LIST OF PUBLICATIONS CHOSEN AS THE BASIS FOR THE PhD PROCEDURE

According to: act on academic degrees and academic title as well as on degrees and title in the field of art (Dz.U. 2003 Nr 65 poz. 595) – 2, *a doctoral dissertation may be prepared in the form of a typescript of a book, published book or a thematically coherent set of chapters in published books, coherent collection of articles published or accepted for publication in scientific journals, defined by the minister responsible for science on the basis of regulations on financing science* (...).

No.	**Publications**	**ME&S points**	**IF$_{2020}$**	**Individual output**
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**	100	6.953	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**	100	5.118	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**	100	4.282	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**	70	1.213	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**	100	5.909	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**	200	7.963	60%

$\Sigma_{ME\&S}$ *points* = 670 Σ_{IF2020} = 31.438

3. ABSTRACT

The results gathered in the presented PhD thesis focus on two pathways of biopolymers utilization. The first route deals with evaluating new sources of chitin in sponges (phylum Porifera), specifically Demosponginae class. Consequently, the publications entitled **The demosponge *Pseudoceratina purpurea* as a new source of fibrous chitin** (**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. *Int. J. Biol. Macromol.* (2018) 112: 1021–1028) and **First report on chitin in non-verongiid marine demosponge: The *Mycale euplectellioides* case** (**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. *Mar. Drugs* (2018) 16: 68) aim to investigate, for the first time, the presence of chitin in species *P. purpurea* and *M. euplectellioides.* The chitin isolation was performed using the standard approach of sodium hydroxide based demineralization, followed by decalcification and desilicification. Subsequently, isolated scaffolds were thoroughly investigated using various techniques, including calcofluor white staining, FTIR analysis, electrospray ionization mass spectrometry (ESI-MS), scanning electron microscopy (SEM), fluorescence microscopy, and chitinase digestion test. The studies confirm with solid evidence the presence of alpha-chitin in the skeleton of both sponges. Nevertheless, the discovery of chitin within the representatives of verongiid sponge *P. purpurea* and non-verongiid sponge *M. euplectellioides* opens new perspectives on the development of renewable sources of both chitin and biologically active metabolites, which have great potential to be used in biomedicine, pharmacology, and tissue engineering.

The second path of the presented thesis focused on applying spongin-based scaffolds isolated from commercial sponges to obtain novel hybrid materials based on either carbonized spongin scaffolds or spongin itself. Likewise, the thermal degradation kinetics of spongin was investigated to evaluate the potential of this biopolymer to be a new source of structured biocarbons. Therefore, in work entitled **Thermal decomposition behaviour and numerical fitting for the pyrolysis kinetics of 3D spongin-based scaffolds. The classic approach** (**Żółtowska S.,** Koltsov I., Alejski K., Ehrlich H., Ciałkowski M., Jesionowski T. *Polym. Test.* (2021) 97: 107148) the values of activation energy E_A, pre-exponential factor A and form of function $f(\alpha)$ were

investigated based on data obtained from thermogravimetric analysis (TG). Various mathematical approaches such as Coats–Redfern method and the model-free iso-conversional Friedman, Kissinger–Akahira–Sunose (KAS), and Ozawa–Flynn–Wall (OFW) methods were used to calculate the values of kinetic parameters. Moreover, based on the theory of the active complex of reagent, the changes of entropy (ΔS), enthalpy (ΔH), and free Gibbs energy (ΔG) were computed. For the first time, this study takes up the challenge of describing the pathway and course of thermal degradation of spongin owing to the physicochemical properties of spongin and biocarbons.

Further studies evaluate the potential of spongin-based skeletons in the preparation of advanced hybrid materials. Thus, the immobilization of silver and cobalt was performed to obtain novel composites, as described in the publication entitled **Commercial sponges in heterogeneous catalysis: developing novel composites with cobalt and silver (Żółtowska S.,** Modelska M., Piasecki A., Jesionowski T. *Physicochem. Probl. Miner. Process.* (2020) 56(6)). The effectiveness of functionalization was evaluated using various techniques, including scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDS), Fourier-transform infrared spectroscopy (FTIR), and thermogravimetric analysis (TG). However, the main point of that study was applying prepared composites as a catalyst in the reduction reaction of 4-nitrophenol with 4-aminophenol in the presence of sodium borohydride in the aqueous environment. The obtained results showed high catalytic activity of prepared materials with significant stability during repetitive reuse. Moreover, structural studies of spent catalysts showed no visible changes in their morphology.

Finally, the possibility of preparation of advanced structured biocarbons from spongin was comprehensively studied. For this reason, low-temperature carbonization was carried out at temperatures 400 °C, 500 °C, and 600 °C. The resulting biocarbons were used as a support and functionalized with cobalt oxide and nickel hydroxide, nickel oxide, and metallic nickel phases by the simple sorption-reduction method. The structure and chemical composition of the prepared materials, as well as biocarbons, was deeply investigated employing various analytical techniques, including transmission electron microscopy (TEM), SEM with EDS, FTIR, X-ray photoelectron spectroscopy (XPS), X-ray fluorescence spectroscopy (XRF) low-temperature nitrogen sorption, and X-ray diffraction (XRD). Further, obtained composites were tested as potential catalysts in various oxidation-reduction reactions.

The carbonized spongin based scaffolds functionalized with cobalt oxide described in work entitled **Three-dimensional commercial-sponge-derived Co_3O_4@C catalysts for effective treatments of organic contaminants** (**Żółtowska S.,** Minambres J.F., Piasecki A., Mertens F., Jesionowski T. *J. Environ. Chem. Eng.* (2021) 9: 105631) were successfully applied in the oxidation of styrene, decolorization of rhodamine B dye and reduction of 4-nitrophenol. It was shown that fibrous structure with open porous canals provides good accessibility for substrates to the surface of the catalysts, resulting in high catalytic activity. Reusability studies proved good activity even after the fifth catalytic cycle in both oxidation and reduction reactions.

The composites obtained after functionalization with nickel species described in the publication **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** (**Żółtowska S.,** Bielan Z., Zembrzuska J., Siwińska-Ciesielczyk K., Piasecki A., Zielińska-Jurek A., Jesionowski T. *Sci. Total. Environ.* (2021) 794: 148692) showed significant activity in the oxidation of phenol, 4-chlorophenoxyacetic acid (4-CPA) and methylchlorophenoxypropionic acid (MCPP) as well as reduction of 4-nitrophenol. The mechanism of reactions was discussed, and the support's effect on catalytic properties was evaluated in detail.

Spongin-based scaffolds show great potential to be used to produce three-dimensional composites for various applications. Moreover, the kinetically favorable carbonization of those scaffolds leads to obtaining structured materials that can be easily modified with a metal-containing phase having impressive catalytic performance in the treatment of emerging compounds.

4. STRESZCZENIE

Otrzymane rezultaty w ramach zrealizowanej pracy doktorskiej dotyczą dwóch nurtów poznawczych wykorzystania biopolimerów. Pierwsza ścieżka związana jest z poszukiwaniem nowych źródeł chityny w gąbkach (typu Porifera), a konkretnie w klasie Demosponginae. W konsekwencji powstały publikacje **The demosponge *Pseudoceratina purpurea* as a new source of fibrous chitin** (**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. *Int. J. Biol. Macromol* (2018) 112: 1021–1028) oraz **First report on chitin in non-verongiid marine demosponge: The *Mycale euplectellioides* case** (**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. *Mar. Drugs* (2018) 16: 68) opisujące po raz pierwszy obecność chityny w wybranych gatunkach gąbek morskich *P. purpurea* i *M. euplectellioides*. Izolację chityny przeprowadzono stosując standardową metodę demineralizacji wodorotlenkiem sodu, a następnie dekalcyfikacji i desillifikacji. Chitynowy biopolimer w wyizolowanych szkieletach został potwierdzony przy zastosowaniu różnych technik badawczych, m.in. takich jak: barwienie metodą Calcofluor White, spektrofotometria FTIR, spektrometria masowa z jonizacją przez elektrorozpylanie (ESI-MS), skaningowa mikroskopia elektronowa (SEM), mikroskopia fluorescencyjna i enzymatyczne trawienie chitynazą. Na podstawie uzyskanych rezultatów i ich analizy jednoznacznie potwierdzono odkrycie alfa-chityny w szkieletach obu gąbek. Należy podkreślić, że to odkrycie otwiera nowe perspektywy rozwoju odnawialnych źródeł zarówno chityny, jak i biologicznie aktywnych metabolitów, które mają ogromny potencjał aplikacyjny w biomedycynie, farmacji i inżynierii tkankowej.

Druga ścieżka zaprezentowana w omawianej dysertacji doktorskiej koncentrowała się na zastosowaniu sponginy pozyskanej z komercyjnych gąbek morskich, celem uzyskania nowych materiałów hybrydowych opartych zarówno na szkieletach sponginowych oraz na karbonizowanych rusztowaniach sponginowych. Dlatego ważnym elementem prac było wyznaczenie kinetyki termicznej degradacji sponginy, aby ocenić potencjał tego biopolimeru jako nowego źródła strukturyzowanych biowęgli. W pracy zatytułowanej **Thermal decomposition behaviour and numerical fitting for the pyrolysis kinetics of 3D spongin-based scaffolds. The classic approach**

(**Żółtowska S.,** Koltsov I., Alejski K., Ehrlich H., Ciałkowski M., Jesionowski T. *Polym. Test.* (2021) 97: 107148) określono wartości liczbowe energii aktywacji E_A, współczynnika przedwykładniczego A, jak również postać funkcji f(α), na podstawie danych uzyskanych z analizy termograwimetrycznej (TG). Do obliczenia wartości liczbowych parametrów kinetycznych wykorzystano kilka metod matematycznych, takich jak metoda Coatsa-Redferna i bezmodelowa izokonwersyjna metoda Friedmana, Kissingera-Akahira-Sunose (KAS) oraz Ozawa-Flynn-Wall (OFW). Ponadto, w oparciu o teorię aktywnego kompleksu, obliczono wartości zmiany entropii (ΔS), entalpii (ΔH) oraz swobodnej energii Gibbsa (ΔG). W pracy po raz pierwszy podjęto wyzwanie opisania szlaku i przebiegu termicznej degradacji sponginy z uwzględnieniem właściwości fizykochemicznych zarówno sponginy jak i biowęgli.

Dalsze badania prowadzono pod kątem oceny potencjału użytkowego szkieletów sponginowych w przygotowaniu zaawansowanych materiałów hybrydowych. W związku z tym przeprowadzono immobilizację srebra i kobaltu w celu uzyskania nowych kompozytów, jak opisano w publikacji pt. **Commercial sponges in heterogeneous catalysis: developing novel composites with cobalt and silver (Żółtowska S.,** Modelska M., Piasecki A., Jesionowski T. *Physicochem. Probl. Miner. Process.* (2020) 56(6): 89–100). Skuteczność funkcjonalizacji szkieletów sponginowych oceniono przy użyciu różnych technik, w tym skaningowej mikroskopii elektronowej (SEM) z dyspersyjną spektroskopią rentgenowską (EDS), spektroskopii w podczerwieni z transformacją Fouriera (FTIR) oraz analizy termograwimetrycznej (TG). Jednak głównym celem tych badań było zastosowanie przygotowanych kompozytów jako katalizatorów w reakcji redukcji 4-nitrofenolu do 4-aminofenolu w obecności borowodorku sodu w środowisku wodnym. Na podstawie uzyskanych wyników potwierdzono wysoką aktywność katalityczną przygotowanych materiałów o znacznej stabilności podczas wielokrotnego ponownego użycia. Ponadto badania strukturalne zużytych katalizatorów nie wykazały widocznych zmian w ich morfologii.

Finalnie wszechstronnie i kompleksowo określono możliwość przygotowania zaawansowanych, strukturyzowanych biowęgli ze szkieletów sponginowych. W tym celu prowadzono niskotemperaturową karbonizację w temperaturach 400, 500 i 600 °C. Otrzymane biowęgle wykorzystano jako nośniki fazy metalicznej. Dokonano funkcjonalizacji karbonizowanych szkieletów sponginowych tlenkiem kobaltu oraz wodorotlenkiem niklu, tlenkiem niklu i metalicznym niklem wykorzystując prostą metodę sorpcji i redukcji. Strukturę i skład chemiczny przygotowanych materiałów, a także biowęgli dokładnie scharakteryzowano wykorzystując w tym celu transmisyjną mikroskopię elektronową (TEM), skaningową mikroskopię elektronową (SEM), dyspersyjną spektroskopię rentgenowską (EDS), spektroskopię w podczerwieni z transformacją Fouriera (FTIR), rentgenowską spektroskopię fotoelektronów (XPS), rentgenowską spektroskopię fluorescencyjną, niskotemperaturową sorpcję azotu oraz dyfrakcję rentgenowską (XRD). Ponadto otrzymane kompozyty przetestowano jako potencjalne katalizatory w różnych reakcjach utleniania-redukcji.

Materiały sfunkcjonalizowane tlenkiem kobaltu opisane w pracy pt. **Three-dimensional commercial-sponge-derived Co_3O_4@C catalysts for effective treatments of organic contaminants** (**Żółtowska S.,** Minambres J.F., Piasecki A., Mertens F., Jesionowski T. *J. Environ. Chem. Eng.* (2021) 9: 105631) zostały z powodzeniem zastosowane w reakcjach utleniania styrenu, odbarwiania barwnika rodaminy B i redukcji 4-nitrofenolu. Wykazano, że włóknista struktura katalizatorów z otwartymi kanałami porowatymi zapewnia dobrą dostępność substratów do powierzchni katalizatorów, co skutkuje wysoką aktywnością katalityczną. Dodatkowo w badaniach nad możliwością ponownego wykorzystania wykazano dużą aktywność tych materiałów nawet po piątym cyklu katalitycznym, zarówno w reakcjach utleniania, jak i redukcji.

Kompozyty otrzymane po funkcjonalizacji związkami niklu zostały opisane w publikacji **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** (**Żółtowska S.,** Bielan Z., Zembrzuska J., Siwińska-Ciesielczyk K., Piasecki A., Zielińska-Jurek A., Jesionowski T. *Sci. Total. Environ.* (2021) 794: 148692). Rezultaty badań wskazały znaczną aktywność opisywanych materiałów w utlenianiu fenolu, kwasu 4-chlorofenoksyoctowego (4-CPA) i kwasu metylochlorofenoksypropionowego (MCPP) oraz redukcji 4-nitrofenolu. Omówiono mechanizm reakcji oraz szczegółowo oceniono wpływ nośnika na właściwości katalityczne.

Szkielety sponginowe wykazują ogromny potencjał ich wykorzystania do produkcji trójwymiarowych kompozytów o szerokiej gamie zastosowań. Co więcej, kinetycznie korzystna karbonizacja tych rusztowań prowadzi do otrzymania strukturalnego materiału węglowego, który można łatwo modyfikować fazą zawierającą metal. Dzięki temu możliwe jest uzyskanie w prosty sposób materiałów o imponujących właściwościach katalitycznych.

5. INTRODUCTION

5.1. Biomimetics in materials science – state of the art

Nature always finds a way. The paraphrase of this one of the most iconic pop culture quote constitutes a proper introduction to the biomimetic topic. Since ancient times nature has been a constant inspiration and a driving force of the development of humankind. Nature also provides us with essential, however elementary, tools and materials that generations are using to develop the most complex inventions. Moreover, the materials and structures of biological origin usually are built from the fibers or the various types of receptor systems. Thus, even the most complex and hierarchical organizations can be created. While treated as an engineering sketch, the living beings and natural products, contrary to human-build designs with strictly specified properties and prepared as exact duplicates, have regular features and operate well even if they exhibit some differences within the same species. On the other hand, exact duplicates' production is a deliberate act to obtain the product with strictly designed quality [1].

As a result of the centuries of observations of nature and utilizing its products, the approach of preparing materials and/or systems inspired by nature was called biomimetic. Even though the biomimetic concept has been known for centuries, just in 1957, Otto H. Schmitt first used the term biomimetics to describe studies dealing with mimicry of nature's mechanisms, processes, and methods [1–3]. According to the definition provided by Janine Benyus, this term refers to *"studying nature's most successful developments and then imitating these designs and processes to solve human problems. It can be thought of as 'innovation inspired by nature"* [4]. Although the term biomimetics became established in the scientific literature relatively recently, the concept has been in use for centuries [5].

A prominent example is the preparation of artificial silk by the Chinese more than 300 years ago [6]. Since that time, people have been seeking the solution in nature. Leonardo da Vinci was inspired to design planes and ships by observing the birds and fishes [7]. The plane's project made by the Wright brothers was built upon an observation that birds do not move their wings always, instead of sliding upon the air current. Another representative example of biomimetics in science is the textile product - the hook and loop fastener called Velcro, developed by Swiss inventor George de Mestral. He was inspired by the burrs and their hook-like construction, which he found fixed on his trousers and dog's fur. In the late sixties of the XX century, the exhaustive study resulted in developing new branches derived from biomimetics. The history of the development of biomimetics studies is gathered in Fig.1.

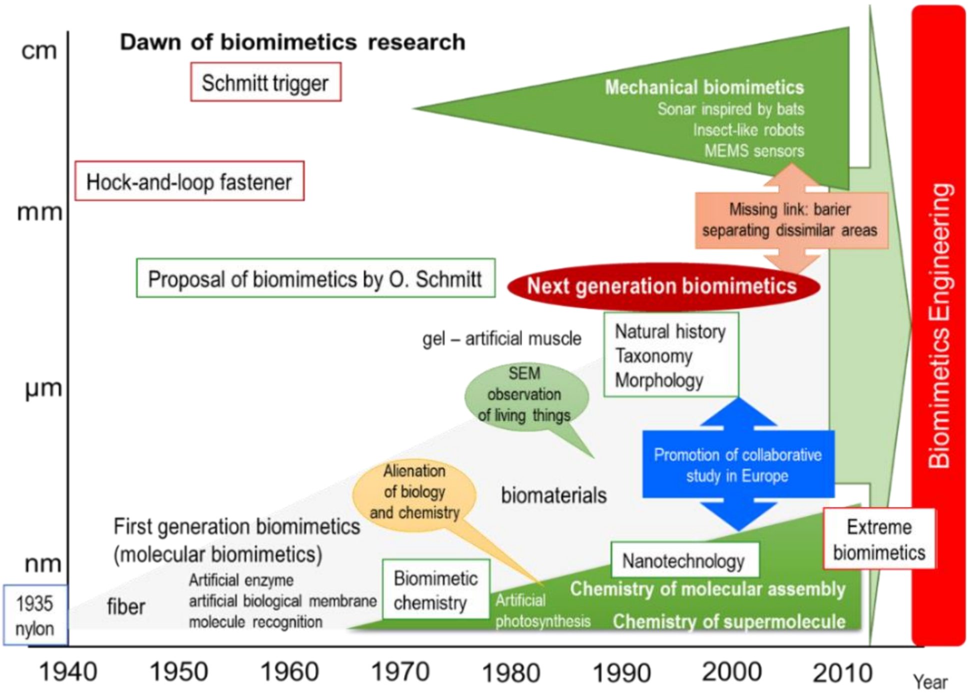


Fig. 1. *The history of biomimetics, based on [8].*

First-generation biomimetics studies were related to molecular biomimetics and the development of enzymes and bio-membranes at the molecular level [8]. Then the artificial photosynthesis research has been active since the dye-sensitive solar cells were developed. However, the establishment of molecular biology has turned biology into the mainstream to follow evolution and life phenomena. At the same time, the biomimetic chemistry was turned into bio-inspired materials chemistry [7,9], which covers a wide array of topics, including the design, synthesis, and development of biologically inspired complex, hierarchical materials on a nano-, micro-, or even macro-scale, and the self-assembly of small molecules [10]. Essential to notice as an example is a material based on the skin concept of sea cucumbers [6]. The skin of sea cucumbers can change the stiffness from low to high within a few seconds. This is possible due to developing a nanocomposite where collagen fibers reinforce a low-module matrix. The biomimetic/bio-inspired materials seem to be promising for designing novel composites for regenerative medicine, bionic and orthopedic devices. Especially those which for the external stimulus answer with the change of mechanical properties or self-healing or self-assembly properties. Another prominent example is one of the most water-repellent surfaces in nature – the leaf of the lotus plant. By the observation of the surface structure of the leaf, it was possible to develop the simple waxy-hydrophobic material with exceptional anti-wetting properties. Such coatings are used to reduce drag on ship hulls, stain- and water-proof fabrics, and improve separation processes in mining industries [8].

Within the biomimetic studies, the particular interest is also paid for the association of biopolymers with inorganic molecules to create remarkable biominerals similar to bone, frustules of diatom, seashells, among others, the assembly of mineral content shape, structure, and size can be controlled. The bioinorganic materials constitute an inspiration for many scientists worldwide. This curiosity is related to the fact that simple inorganic materials like silicon dioxide (SiO_2), iron sulfate ($Fe_2(SO_4)_3$), or calcium carbonate ($CaCO_3$) are structured into various complex assemblies which are durable and tough. Therefore, the formation of numerous ceramic-polymer hybrid materials by utilizing inorganic solids to mimic these natural architectures' molecular interactions seems to be a promising possibility and solution for developing the novel class of functional materials.

The seventies of the XX century can be considered the most groundbreaking in developing various branches of biomimetics [8-10]. In this decade, studies have blossomed in mechanics and fluid dynamics fields, which resulted in the development of robots that mimic the movement of insects, fish, dogs; sensors based on insects' hairs and radars and sonars that use the echolocation capabilities of baths. Consequently, a new branch of studies arises called bionics. However, it should be mentioned that terms bionics and biomimetics are currently considered synonyms because both originate from observing the system that exists in nature [1]. Nevertheless, such studies continue without decline until now, mainly in the military, ships, railways, and astronautic industries.

However, in the last decade, a meaningful branch of science has emerged from biomimetics. In 2010 in Germany, Professor Hermann Ehrlich established Extreme Biomimetics as a new modern biomimetics field [11–13]. It is a multi- and interdisciplinary research area, where various science fields, i.e., biology, chemistry, physics, and materials science, forgather. This research area is gaining importance in designing a new generation of hybrid materials with a three-dimensional, hierarchical structure, using methods that mimic extreme environmental conditions (such as high or low temperatures, high pressure). Extreme Biomimetics's primary goal is to understand the mechanisms and principles underlying the biomineralization processes in organisms adapted to living in extreme conditions. Thus, it will allow for the implementation of established key principles of Extreme Biomimetics in the context of the synthesis of novel biomaterials with a wide range of commercial applications. Another turning point is identifying the biomolecules that play a crucial role in the nucleation processes and control inorganic crystals' growth. The exceptional thermal stability and ability to complex metals by various biopolymers, including polysaccharides (cellulose, pectin, chitin) and proteins (spongin, silk fibers), is evidence that the selected biopolymers can be successfully used as organic matrices controlling the crystallization process of the inorganic phase in the hydrothermal phase [11,12].

Extreme biomimetics principles have been applied in modern materials science for a decade. Various organic-inorganic composites have been synthesized during this time [14-19]. In general, the biopolymers of natural origin were taken for the synthesis of advanced composites. The possibility of obtaining three-dimensional chitin skeletons from marine sponges was the main inspiration for their use in synthesizing advanced hybrid materials [14,15]. This property opens the way for using well-known solvo- and hydrothermal synthesis methods, considered classical for preparing new, nano-structured inorganic-chitin composites [16]. In 2013, a two-step functionalization of the two-dimensional chitin skeleton of Poriferan origin using the micro- and monodisperse Stöber silica was described for the first time. The obtained hybrid materials were characterized by the presence of spherical SiO_2 particles evenly distributed on the chitin fibers, which probably results from the compatibility of Si-OH groups with the hydroxyl groups of chitin [17]. The obtained results were vital for applying the hydrothermal method to obtain an innovative composites following Extreme Biomimetics. In further research, hydrothermal treatment was applied to modify chitin isolated from the skeleton of *Aplysina aerophoba* (Demospongiae; Verongiida; Aplysinidae) marine sponge, with zirconium dioxide [12]. The β-chitin isolated from the skeletons of marine cephalopods of the *Sepia officinalis* was also used as a matrix for forming ZnO crystals *in vitro* under hydrothermal conditions – accordingly to the Extreme Biomimetics rules. The presented results confirmed that this approach allows for the development of inorganic-organic, nano-structured hybrid materials based on β-chitin with special antibacterial properties, which gives excellent prospects for the development of inorganic-organic chitin-based wound-dressing materials [11]. Another prominent example is shown with synthesizing the α-chitin-GeO_2 composite. The resulting α-chitin-GeO_2 composite was characterized by several physical properties, such as enhancing photoluminescence properties, exceeding the previously noted values for other GeO_2-based biomaterials. Such a result suggests that the three-dimensional chitin-based composites can successfully be used to prepare a new generation of diodes and biosensors [18]. Extreme Biomimetics is also a valuable tool for preparing multiphase composites such as chitin-$(Ti,Zr)O_2$ obtained by functionalization of chitin of *Aplysina aerophoba* origin [16]. Moreover, pectin was modified with the germanium oxide with hydrothermal treatment following this approach. Resulted material exhibited good antibacterial properties against various pathogens [19].

Within biomimetics studies, the biomimicry approach must be mentioned as well. However, many literature sources provide information that biomimicry is a synonym of biomimetics; historically, both movements had different goals and underlying connotations. Biomimicry means learning from nature, while biomimetics denotes the field of study in which concepts and designs are applied. In 1997 Janine M. Benyus published her book *Biomimicry*, where the biomimicry term was defined as the emulation of nature's time-tested patterns and strategies to solve human engineering and life challenges [4]. It must be mentioned that within the broad term of biomimicry, several classes can be distinguished (Table 1).

Table 1. *The class of biomimicry.*

Biomimicry class	Definition	Example	Reference
Functional biomimicry	physical and/or chemical properties are inspired by nature	false teeth made from ivory	[20]
Molecular biomimicry	taking inspiration from the types and pathways of atoms and molecules, acquiring them, usually from natural resources, and finally, preparing versatile materials	producing liquid crystals based on a filamentous phage	[21]
Process biomimicry	the mimicking of mechanisms or pathways of conformation of molecules or/and atoms in final products	production of synthetic silk	[22]
Structure biomimicry	taking inspiration from nature in the nano- or microstructure, i.e., molecular organization – of produced materials	foam materials, honeycomb structures	[23,24]

However, the axiom revealing common characteristics of biomimetic materials and biomaterials science is related to restoring natural function while the original material is missing or cannot work properly and sustain the optimal environment for the process. Consequently, biomimicry may give essential clues for every production step, including the molecule's selection and method of biomaterial fabrication [8,25]. Biomimicry is, indeed, a source of inspiration during the design and modification of biomaterials and biomedical devices.

However, it must be mentioned that it is not a panacea to produce biomaterials despite the usefulness of biomimetics. Moreover, it has some limitations, which must be understood to use biomimetics effectively [26,27]. The most critical limitation is the proper understanding of biomimetics and biomimicry – which does not mean literal bio-duplication. The mimicking of nature is related to selective observation, taking inspiration from nature. As in plane design, even though birds are always flapping with their wings during flight, the engineers adapt only the wings and adapt the wing's variable curvature to obtain a compromise between the lift drag over in a wide range of speeds. In another example, nature also produces toxic substances. Therefore, engineers must recognize decent nature's lessons and copy them in a proper context. Another common mistake is related to believing that nature always proposes the best solutions. Regardless of their impressive performance in many ways, natural materials and approaches are not always and must not be better than artificial materials. Biomaterials cannot be used as a substitute for processes operated at high temperatures (200 °C and higher, depending on the material) or/and in chemically harsh conditions – due to the presence of organic matrix. Despite the biomineralization processes involving metallic particles growing in the living organism, biomaterials literally do not synthesize metallic phases. For the purposes where such metallic constructs are essential, biomaterials without proper functionalization are not the best solutions. However, combining the biomaterials and metal-containing phase or synthetical polymers to produce the advanced composites fits the biomimetics approach, although, cannot be called biomimicry [28–30].

Another leading example of biomimetics in material science is a honeycomb structure (Fig. 2) [31,32]. Bees produce this structure due to its efficient configurations, low weight, and high resistance. The honeycomb structure is built from uniformly distributed double-layered hexagonal cells constructed from plant resins named beeswax and propolis [31].

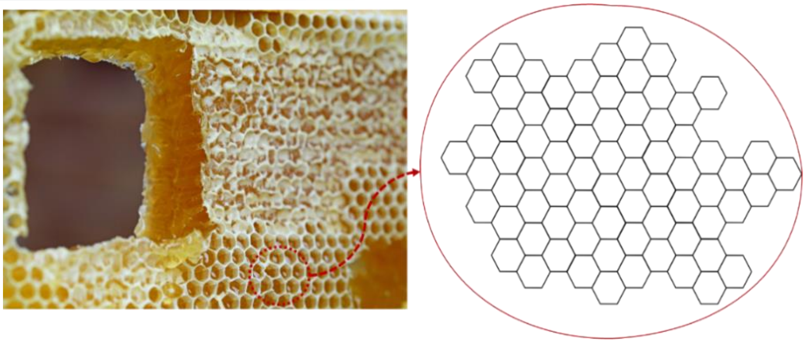


Fig. 2. The piece of honeycomb with an example of the hexagonal pattern, based on [31].

Interestingly, the honeycomb structures have not been investigated and incorporated into material science till the beginning of the XX century; after that, various metallic [33], paper [34], ceramics [35], and composite materials [36] with honeycomb structure have been evaluated. However, the big explosion of interest in this particular structure began in 1999. Hales showed how bees build hives to create the maximum cell space using the minimum amount of beeswax; thus, it was proved that the honeycomb structure is one of nature's most stable structures [37]. After this groundbreaking discovery, the XIX century resonates with the development of materials with a honeycomb structure for engineering fields, nano-, and biomedical sciences. Activated carbon honeycombs [38], photonic bandgap honeycombs [39], microporous arrays in polymeric films [40] are successfully developed via advanced methods [25,41,42]. Nevertheless, with the development of microscopic technologies, new structures similar to honeycombs have been found in nature. A significant amount of various hexagonal or similar patterns have been discovered in cell aggregates [43], living tissues [42], marine sponge skeletons [24], and big molecules [44]. This most stable structure's unique properties have opened wide properties to develop novel, advanced materials for emerging applications ranging from 2 nm until 1 mm [31,32].

The continued study of structure-function relationships in biologically inspired materials and mimicking the strategies and mechanisms observed in nature generate endless possibilities in designing diverse organic and inorganic materials suitable for a wide range of applications [7]. Two seem to be leading among the different reasons for the continually increasing interest in the biomimetic field. Firstly, the regenerative medicine progress results in the increased interest in the preparation of advanced and biocompatible biomaterials with specific structures and properties. Secondly, the recent improvement of characterization and production methods encourages scientists to find how the structure of natural materials, developed by evolution, might be applied to biomimetic engineering projects. Humans have always been learning from nature, and all resulted findings help survive generations and provide a sustainable future.

In summary, the literature emphasizes the scientific and application importance of the biomimetic approach in developing novel materials. Among numerous examples of biomaterials that could serve as the inspiration or precursor for the recreation of functional composite, two potential biomaterials were evaluated in detail within the framework of this thesis. Spongin and chitin of marine sponge origin were chosen to investigate the potential to prepare advanced materials. The mechanical design and design of porous interfaces on nano and micro-levels of chitin-based and spongin-based demosponge scaffolds are applicable for various tissue- and material engineering applications. However, a more detailed justification of their use and functionalization is presented in subsequent chapters.

5.2. Spongin and chitin from sponges as a novel, biomimetic source of biomaterials

Sponges (phylum Porifera) are one of the oldest multicellular organisms, which evolution is dated back to the Precambrian. These simplest animals are distributed either in marine as well as fresh aquatic ecosystems. Based on the genetic and molecular analysis as well as their morphology, the taxonomy of the Porifera phylum contains four classes: Demospongiae, Hexactinellida, Homoscleromorpha, and Calcarea [45]. Despite the taxonomic class, all sponges build their skeletons in various three-dimensional shapes from minerals or organic substances to minimize the metabolic cost and water exchange. Moreover, the skeletons could also be filled out with exogenous materials such as particles of sands or small crustaceans. Most of the Demospongiae and Hexactinellida sponge species have silica-made skeletons containing the silica-based elements named spicules. Their length varies within species between micrometers to centimeters, and they can subsequently interlock or fuse with each other. Besides, the spicules are characterized by high variation in shape and size. Therefore, this feature has gained significant attention in cladistic and taxonomical studies of either living and fossil sponge species. The Calcarea sponges produce mineralized spicules made from calcium carbonate. Thus, their skeletal formations are an excellent example of naturally made, rigid composite calcium carbonate composites.

Currently, there are 11 004 research outputs (state for 1.12.2021) regarding the marine sponges, their biology, chemistry, possible approaches for their utilization, and ecological aspects, which will not be risen in this dissertation. This work pays particular attention to chitin and spongin and their potential to be the biomimetic precursor of valuable materials for material chemistry purposes.

5.2.1. Chitin of sponges' origin

Within the wide range of research regarding the marine sponges, particular attention is paid to representatives of Demosponginae class. Taxonomically this class is the largest among phylum Porifera, including approx. 80% of all living species [45] Demospongiae class is divided into three subclasses: Verongimorhpa, Heteroscleromorpha, and Keratosa. The increasing interest in this class of sponges is related to their unique and characteristic fibrous skeletons made from chitin or spongin as the main organic components.

Chitin, one of the most abundant polysaccharides, has been identified as an evolutionary ancient skeletal construct found in various organisms across the globe [46]. It occurs as crystalline nano- and microfibrils that form structural elements of the exoskeletons of arthropods and in fungal cell walls. Moreover, for other living organisms in the animal kingdom, chitin plays a role in reinforcement and strength protection [46]. From the first successful chitin isolation from mushrooms in 1811 till the present day, this biopolymer has been recognized to build the uni- and multicellular organisms of foraminifera [47,48], diatoms [49,50], hydroids, coelenterates, brachiopods, polychaetes, Pogonophora [51], several species of sponges [52], mollusks [53,54], and crustaceans [55–60], as well as epidermal cuticles of fish [61,62]. The annual chitin estimated natural worldwide production rate was estimated to be approximately 10^{11} tons [46]. However, the material form of chitin is usually a white and complex nitrogenous polysaccharide that is inelastic. On the other hand, chitin is also considered as the emerging source of beach pollution in coastal areas [46].

However, the presence of chitin in representatives of sponges was established relatively late – in 2007 by the discovery of chitin in the skeletal fibers of the demosponge *Verongula gigantea* [63]. The team of Prof. H. Ehrlich proved that the isolated chitin is similar to α-chitin found in invertebrates. This meaningful discovery opens the door for seeking chitin in other representatives of sponges by Prof. Ehrlich's group. Consequently, the chitin has been described in the glass sponge *Farrea occa* [64], species of demosponges of Verongiida order [65–67], Mexican Pacific species of the genus Aplysina and in the sponge *Aplysina fistularis (all belong to verongiids)* [68,69], freshwater demosponge *Spongilla lacustris* [70], holdfast of freshwater demosponge *Lubomirskia baicalensis* [71], Ochridaspongia [72] and as well as heavily mineralized Verongiida demosponge *Suberea clavata* [73]. Moreover, recently the presence of chitin has also been confirmed in another representative of the order Verongiida, *Pseudoceratina purpurea* [74], and non-Verongiida marine demosponges from the family Poecilosclerida: *Acarnus wolffgangi*, *Echinoclathria gibbosa* [75], and *Mycale euplectellioides* [76]. Those studies provide evidence about chitin existence and focus on the evolutionary aspect, where the hypothesis about chitin formation has been proposed [52].

Moreover, the ecological importance of chitin in the marine environment should also be mentioned. According to Johnstone, carbon and nitrogen could rather disappear from the ocean if chitin would not return in biologically functional form because those two elements are limited in the marine ecosystems [77,78]. Globally, the majority of chitin is produced in or near the aquatic environment. The annual production is balanced by the chitin degradation making possible cycling of nutrients in the oceans [79].

Consequently, the worldwide abundance of chitin makes this biopolymer a perfect candidate for application in biomimetics and materials science studies. The versatility of its use is related to easy processible into different products, such as hydrogels [80], membranes [81,82], nanofibers [83,84], beads [85], micro/nanoparticles [80,86], scaffolds [87] and foams [80]. Furthermore, the high porosity, predictable degradation rate, biodegradability, structural integrity, non-toxicity to cells, and biocompatibility made chitin the perfect candidate to fabricate novel, biomedical composite materials [80]. However, to produce such advanced materials, chitin isolation must be carried out by adjusting the approach to the source of chitin. However, all methods are focusing on the removal of protein that binds chitin chains together and minerals. Depends on the chitin source, sometimes a decolorization is carried out to remove the additional pigments. Over the years, numerous methods have been applied and developed for chitin production. However, the chemical and biological methods are principal, among others described in literature [52]. Detailed investigations regarding the methods of chitin isolation from various sources have been gathered elsewhere [46,88]. Industrially, chitin is obtained from crustaceans’ shells in the form of flakes, microparticles, and powders. In that form, chitin is used to produce chitosan, but for the production of 3D scaffolds for tissue engineering or material science purposes, the other, often more expensive processes of forming 3D structures are needed [52].

The chitin isolated from demosponges has fibrous, tubular 3D morphology, with various channels possessing swelling abilities. Such constructs can reach up to 50 μm in diameter, exhibiting the capillary effect. These properties distinguish chitin isolated from demosponges from chitin obtained commercially from crustaceans [52]. Likewise, proved higher thermal stability of demosponges chitin (up to 400 °C) [52] than fungal chitin makes demosponges a prime source of chitin over other commonly developed. Because marine sponges can be cultivated, they can be considered a 3D, naturally prefabricated chitin source. Consequently, chitin of sponges' origin is a promising and ready-to-use 3D scaffolding material with vast possible applications in biomedical and material sciences purposes. Therefore, seeking new species of sponges with skeletons built from chitin is essential not only from a systematic point of view but also for searching for new potential sources of three-dimensional chitin structures.

Within the aim of the presented PhD thesis, the new sources of chitin were discovered and described, showing that chitin preserved the structure of the sponge skeleton and might be applied as ready-to-use scaffolds for various applications (**Publications 1 and 2**). The detailed investigation of chitin isolation is described in the chapter 6 of the presented thesis.

5.2.2. Spongin

Within Demosponginae class, particular attention has also been paid to the utilization of spongin - biopolymer building the skeletons of Demosponges from the Dictyoceratida and Dendroceratida orders – commonly referred to as "keratose or horny sponges" [89,90]. Interestingly, their skeletons do not possess the siliceous spicules – but only proteins: spongin as a main organic component, and often collagen, which is the intercellular organic framework [89].

Although, prior to a detailed discussion, attention should be paid to the definitions of basic terms, including *commercial sponges, sponges*, and *sponge skeletons.* As stated by Jesionowski et al. [91], a *commercial sponge* is a skeleton build from spongin. In contrast, the term *skeleton* means cell and tissue free, dried, demineralized, and depigmented skeletal construct, and finally, term *sponges* refer to the whole organism: body and skeleton.

In the presented dissertation, the spongin derived from the *Hippospongia communis* species was used. Spongin is considered a point of interest due to its thermal stability, unique, fibrous, three-dimensional morphology, and the presence of various heteroatoms (nitrogen, sulfur, iodine, bromine) in its structure [91]. Moreover, the keratosa sponges can be considered as a renewable source of spongin. Nowadays, sponge farming is an established business line, where China, Europe, and North America are considered significant players. The global Natural Sea Sponge market is constantly growing, starting from 20 million USD at the beginning of the XX century. The world sponge market is under constant evaluation, which started in 1980 when the natural sponges started to be cultivated for commercial purposes [91]. Currently, the cosmetics and baby care markets are the primary natural sponge users and generate most of the market.

Furthermore, the COVID-19 pandemic seems to have an impact on the increase of demand in this market. Nevertheless, such impact might be visible in the following years. Likewise, commercial sponges have also become an interesting source of biomaterials for modern biomimetics and material science. Therefore, they seem to have the potential to be implemented to prepare advanced supports for catalysis purposes. Considering the increase in scientific paper publication regarding marine sponges' and spongin application in the past 10 years (see Fig. 3), evaluating their potential seems to be a natural step.

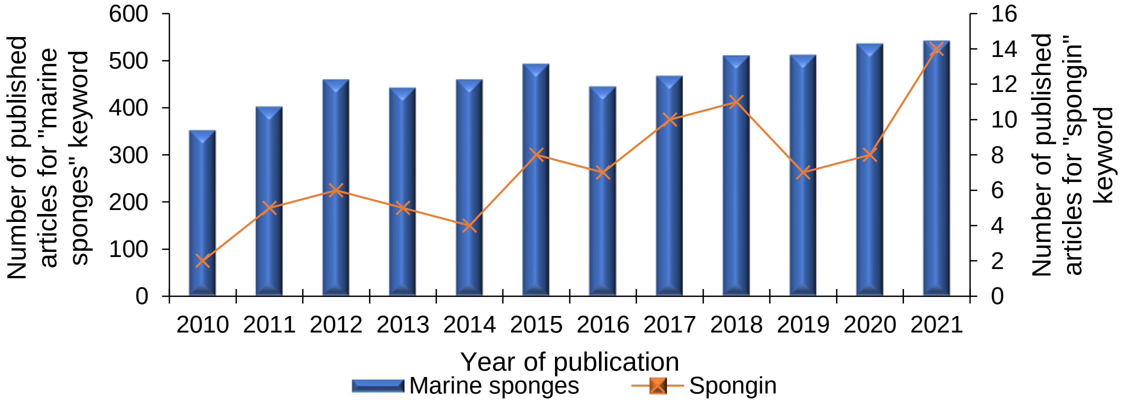


Fig. 3. *The number of scientific articles in the Scopus database for the keywords marine sponges and spongin (date of access: 1.12.2021).*

Interestingly, the detailed chemical composition of spongin is still considered unknown. Nevertheless, it contains the same amino acids already described in collagen and keratin [91]. In some sources, it can be found that spongin is defined as a collagenous protein typical for sponges. For a better overview, the gathered information regarding the content of amino acids in various representatives of Keratose sponges is given in Table 2.

Table 2. *The amino acid content in various Demosponges belonging to the Dictyoceratida order.*

Amino acid	**Content calculated per 100 g of spongin**					
	Common bath sponge [92]	*Hippospongia communis* [93]	Common sponge (*Hippospongia* Genus [94]	*Spongia graminea* [95]		Mean value for *Ircinia variabilis*, *Hippospongia communis*, *Cacospongia scalaris* [96]
				Spongin A	Spongin B	
Alanine		0.2		2.8	5.4	7.9
Arginine		5.9	4.3	5.1	5.4	4.6
Aspartic acid	4.7	4.5		7.4	9.3	10.4
Cystine		Traces	2.8	0.5	1.1	2.0
Diiodotyrosine			Traces			
Glutamic acid	18.1	18.4		8.6	8.9	7.7
Glycine	13.9	14.0	14.4	12.5	15.0	30.0
Isoleucine				1.9	1.6	2.1
Histidine			0.2	0.4	0.4	0.4
Hydroxylysine				1.2	2.8	2.9
Hydroxyproline				8.5	8.6	8.7
Leucine	7.5			2.2	2.2	2.8
Lysine			3.0	0.8	2.5	3.8
Methionine				0.4	0.3	Traces
Phenylalanine			3.3	1.0	1.2	1.3
Proline	6.3	5.7		5.3	5.8	7.3
Serine				2.3	1.7	2.2
Threonine				3.0	2.2	2.3
Tyrosine		2.8	0.8	0.5	0.6	0.5
Valine				2.0	1.9	2.8

As shown in Table 2, the amino acid composition of spongin varies with different sponge species. The deeper discussion regarding the chemical composition, types of spongin, and collagen types associated with spongin, their chemistry, and biology was not in the scope of the presented dissertation. In any case, that information can be found elsewhere [89,90,97].

Going deeper into the elemental composition, the results of recent studies revealed that spongin-based skeletons of *Hippospongia communis* possess a high content of carbon, oxygen, hydrogen, and nitrogen [91]. Moreover, the presence of halogens and other elements such as sulfur, sodium, silicon, calcium, magnesium, or iron has been confirmed using the energy-dispersive X-ray spectroscopy (EDS) technique [91]. Halogens are related to 3,5-diiodotyrosine and 3-bromotyrosine [92], where in Dictioceratida order, halogenated tyrosines exist together with proteinogenic amino acids. Due to the existence of tyrosine compounds, the presence of aromatic carbon has been confirmed using FTIR analysis ([98], **Publication 5** [99]). The presence of sulfur is associated with the existence of cysteine in amino acid chains of spongin – what is the example of similarity of spongin to keratin.

Moreover, the studies performed within the framework of this dissertation and the previous works of the research group confirmed the presence of the low amount of Fe, Si – those elements might be incorporated into the skeletons during the sponge's growth [98–101]. The existence of sodium, calcium, magnesium, aluminum has been proved in other studies and may depend on the environment [102]. Interestingly, as was shown in **Publications 3-6** [99,100,103,104], the cleaning procedure does not remove all materials aggregated in the sponge structure. However, some micro debris or sand particles can be successfully removed.

Despite their unique chemistry, the spongin-based skeletons are an interesting source of biomaterials also from the morphological point of view. The skeletons have a hierarchical, multi-level organization of fibers with thickness varying from few to several micrometers – typically 10-15 μm (**Publication 5** [99]). Those fibers are built from densely packed microfibrils and arranged within a preferential orientation – typically in concentric layers. The diameter of microfibrils has been a measure to be approx. 10 μm [91]. The spongin-based skeletons are three-dimensional, reticular, possessing open-pores cellular structures with multi-junctional regions (Fig. 4).

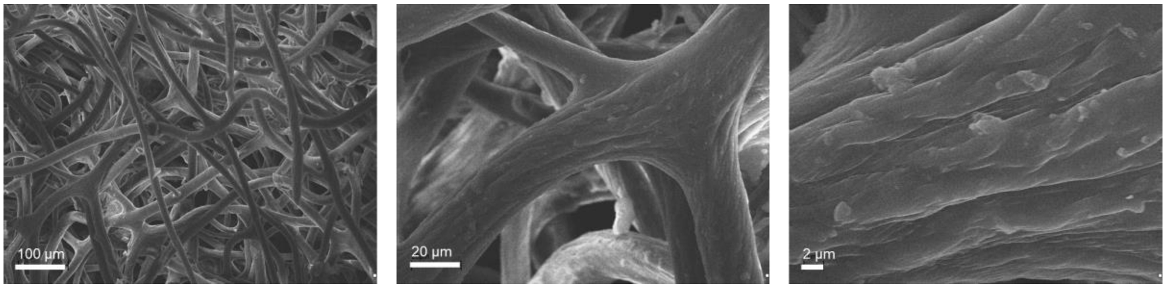


Fig. 4. *SEM images of the spongin-based skeleton from H. communis sponge at different magnifications adapted from* [105].

On the macroscale, the structure of spongin-based scaffolds seems to be favorable compared to other biomaterials. The hierarchical arrangement of fibers that form a system of open channels, often hexagonal in shape, recalls the honeycomb-like structure commonly observed in nature (Fig. 5).

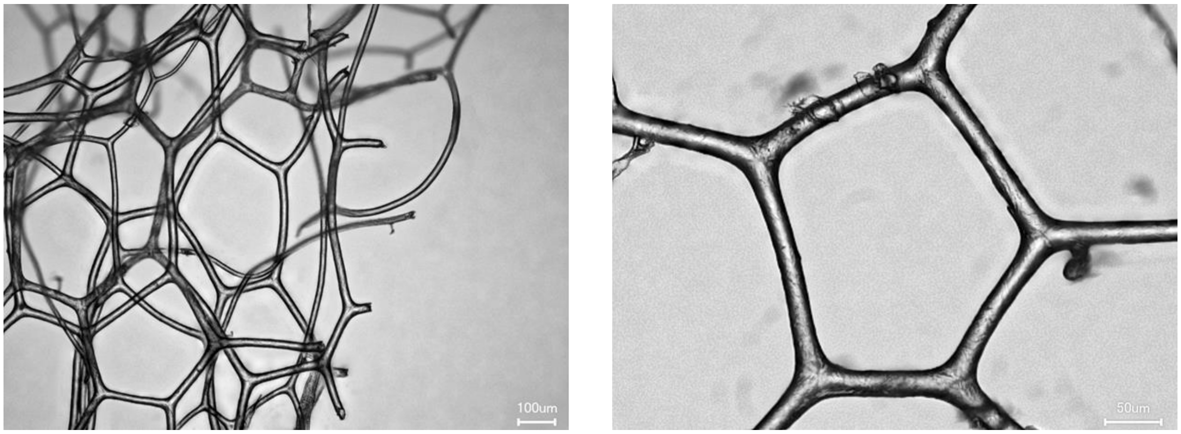


Fig. 5. *Images from the optical microscope of the spongin-based skeleton, showing the fibers arrangement* [98,105,106].

Due to the growing conditions of sponges, where they must face the constant water current, those simple animals developed skeletons that can withstand it. In addition, their high porosity allows for the pumping of vast volumes of water. However, the sponges' skeletons do not ideally resemble the honeycomb structure. The cellular structure exhibits similarities and is a reason for extraordinary mechanical properties at low weight and low density and functional features (such as firmness, elastic limits, compression modulus, rigidity and stiffness, among others) [107]. Nature use such extraordinary strategy in the number of biological systems, including wood, bone, or cork. Nevertheless, these unique properties make spongin an interesting material for use in material science purposes.

Moreover, despite the hierarchical and multi-level organization of fibers and fibrils, the hydrophobic interactions [108] together with various cross-links such as sulfur-sulfur type derived from cysteine and cysteine residues and those between the molecules of the tropocollagen elements and aromatic rings of some amino acids provide the extraordinary skeleton stabilization. The surface area of spongin has been estimated to be 2.5 and 3.4 m^2 for 3 to 4 g per skeleton [91], **Publication 3** [104]. Either way, a detailed investigation regarding the mechanical properties of different Demosponginae representatives has been shown in the work of Louden and co-workers [109].

Interestingly spongin exhibits high resistance toward enzymatic treatment compared to collagen. As an example, spongin is resistant toward enzymatic action of pepsin, bacterial collagenases, chymotrypsin, trypsin, papain, protease, amylase, cellulase, lysozyme, and elastase [108]. Besides the resistance to enzymatic treatment, spongin is also insoluble in acids and can withstand the treatment with 5% trichloroacetic acid at 90 °C [23], similar to keratin. However, the alkaline treatment results in the dissolution of spongin to its amino acids hydrolysates.

Additionally, spongin is thermally stable, as was proved in **Publication 3** [104]; the thermal degradation (in an inert atmosphere) started at a temperature between 140-150 °C, while the particular temperature depends on the heating rate. Such thermal stability is similar to that associated with keratin. On the other hand, similarities with collagen are related to the flexibility and support which gives spongin.

Taking into consideration the features mentioned above and the properties of both spongin and chitin, it is apparent that they can be successfully applied to prepare biologically inspired materials using tools provided by biomimetic and extreme biomimetic approaches. Such prominent examples will be presented in the following chapter.

5.2.3. Application of spongin and chitin derived from marine sponges in modern materials science

Among many possible applications of sponges and their skeletons and metabolites in pharmacy, cosmetic chemistry industry, or tissue engineering within this dissertation, the possibilities for the development of advanced composites will be investigated. The previously mentioned unique properties of spongin and chitin of sponge origin make those biomaterials promising to be used to prepare novel composites with a wide range of possible applications. Numerous attempts have been applied to use the chitin as a functional matrix to prepare advanced composites via Extreme Biomimetic routes, as described in Chapter 5.1 of the dissertation [10-11; 13-15; 17-18].

On the other hand, spongin-based scaffolds were utilized to prepare advanced composite as well. The hydrothermal approach was used to prepare composites of spongin with hematite [110] or titanium dioxide [111], where resulted material had a positive effect on the capacity of energy storage devices and was an effective photocatalyst for the photo-degradation of methylene blue. Spongin-based scaffolds were also used as a support for enzyme immobilization [112]. Moreover, they were functionalized via dyes adsorption to prepare novel hybrid materials with antibacterial [106], antiradical [105], and photocatalytic properties. As an example, spongin–copper-phthalocyanine [101] and spongin–iron phthalocyanine [98] materials showed significant activity in the degradation of phenol, its halogenated derivatives, and rhodamine B. Recently, the functionalization with cobalt and silver via sorption-reduction approach resulted in the preparation of cobalt-, silver, and cobalt-silver-spongin-based composites, which exhibited promising activity in the reduction of 4-nitrophenol (**Publication 4** [103]).

Nowadays, a new trend is developing where the spongin-based skeletons are applied as a source of biomass to prepare structured bio-carbons in an oxygen-free atmosphere. In this manner, several composites have been prepared. For example, MnO_2/carbonized spongin composite was first prepared by simple carbonization of spongin-based scaffolds and further functionalization [113]. Interestingly, the unique structure of spongin preserved carbonization at temperature as high as 650 °C, within the framework of this work, resulting in material exhibited good electrochemical properties, based on the results obtained from cyclic voltammetry. Consequently, preserving the spongin's structure after carbonization at temperature 650 °C encourages scientists to perform carbonization at temperatures as high as 1200 °C [114]. Thereupon, the turbostratically disordered carbon has been obtained with a high surface area [114].

Moreover, the hierarchical, fibrous-like structure – typical for spongin-based skeletons was preserved after carbonization at such a high temperature. Besides, those carbonized scaffolds were characterized by enhanced mechanical properties. Further, its functionalization via electrochemical deposition of copper oxide(I) results in the formation of a three-dimensional catalyst with promising activity towards reducing 4-nitrophenol in simulated seawater and deionized water. Likewise, owing to the properties of spongin-based scaffolds after carbonization, this biomaterial has been tested as potential support for the metal-containing phase after low-temperature carbonization. As a consequence, several composites have been developed based on carbonized spongin-based skeletons at temperatures 400 °C, 500 °C, and 600 °C functionalized with Co_3O_4 (**Publication 5** [99]) and $Ni(OH)_2$/NiO/Ni (**Publication 6** [100]). Those materials have been characterized in detail and tested as potential catalysts in the oxidation-reduction reaction of numerous organic compounds. Both studies proved the potential of low-temperature carbonized spongin-based skeletons in preparing advanced materials for catalytic purposes.

In summary, the current studies unveil just the tip of the iceberg of the application of chitin and spongin to prepare advanced materials. The current findings add substantially to our understanding of the importance of developing novel sources of chitin, which do not require expensive structure formation. Moreover, several noteworthy contributions have been made to applying spongin-based scaffolds in material science, particularly to developing new, advanced heterogeneous catalysts, photocatalysts, and electrochemically active components. The successful attempts to apply spongin-based scaffolds as a precursor of carbonized materials were a primary motivation in further developing this topic in detail. For this reason, the discussion regarding spongin and chitin as the precursor of bio-carbons is evaluated in the next chapter, where an overview of the features, advantages, and disadvantages is given.

5.3. Structured, three-dimensional carbon materials derived from biomass for catalytic purposes

The growing environmental pollution and the rapid increase of population and industrialization force the societies to develop more sustainable routes of further industrial and social development [115,116]. Among many possible solutions to solve the worldwide economic and environmental crisis, the increasing interest in applying biomass and swage to produce the emerging materials seems to be a reasonable pathway [117–119].

Before investigating this topic, the expression of "emerging materials" should be explained. The emerging materials consider a broad variety of composite materials, hybrid materials, carbonaceous, metal, ceramic, polymeric, electronic materials in various forms, shapes, 1D, 2D, or 3D structures, either of organic and inorganic origin [120]. Those materials are an important key for technological industries. However, the seeking of new precursors pursues different properties of these materials, depending on the section. Nevertheless, what means emerging rely upon the industry and the specific application [115].

In the field of heterogeneous catalysis, stability in a wide range of conditions, good mechanical properties, and proper structure are primary constraints. Therefore, carbonaceous materials have become a promising option in the past years, especially for sustainable development and green chemistry. Specifically, biomass utilization for producing carbonaceous materials, even those with specific three-dimensional structures, has attracted particular attention recently [121–125]. The literature analysis from the last decade shows the constant increase of interest in bio-carbons, their synthesis, functionalization, and applications for catalytic purposes. The graph showing the number of Scopus indexed original research articles focusing on bio-carbons is demonstrated in Fig. 6.

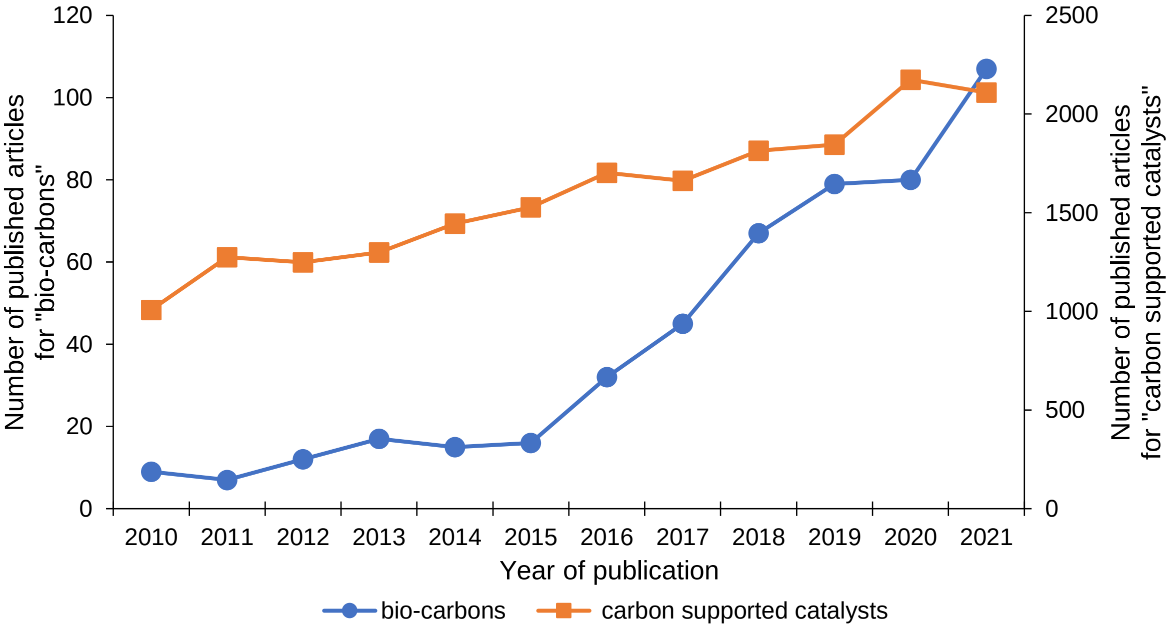


Fig. 6. *The number of scientific articles in the Scopus database for the bio-carbons and carbon-supported catalysts (date of access: 1.12.2021).*

Such materials referred to in the scientific literature as "bio-carbons" are obtained by transformation of the carbon-rich biomass source into a porous material by the artificial processes, including the thermal, hydrothermal carbonization, or templated method [126]. The bio-carbon term has a broad scope and covers various materials: activated carbons, biochar, and hydrochar, among others, where they are produced from biomass [127]. The bio-carbons exhibit advantages over classical carbonaceous materials and other advanced catalytic supports such as zeolites, graphene, or CNT, as follows:

- The biomass materials are cheap and abundant; thus, this feedstock is considered as cost-effective;
- The carbonization under inert gas protection resulted in biomacromolecules skeleton preservation and the formation of interconnected carbon structures with nanopores;
- The versatile precursors can be converted into bio-carbon, applying simple purification, carbonization, and activation procedures. Moreover, various heteroatoms or functional moieties can be introduced during the carbonization to obtain strictly tailored properties;
- The transformation of biomass into bio-carbon is considered an eco-friendly process.

Regarding the last point, opposite to the preparation of carbon nanotubes (CNT), graphene, or mesoporous silicas, the production of structured bio-carbons does not require high pressures or harsh chemicals. Moreover, bio-wastes utilization to produce functional bio-carbons represents a state-of-art of "green-pathway" to produce a new generation of functional materials.

The starting point in preparing any bio-carbon is the proper selection of the precursor, which has a critical influence on the final product's properties and morphology. The good precursor should have a high carbon and other doping elements content, three-dimensional, nanoporous structure to enhance the properties of resulted materials for catalytic purposes. Therefore, it is crucial to have a good understanding of the chemical and elemental composition of biomass, making it possible to predict the composition and structure of bio-carbon. Such huge diversity in bio-carbon precursors leads to the urgent need to develop a general strategy to produce bio-carbons with strictly tailored content of heteroatom doping, structure, and porosity.

Different biomass types have been utilized to fabricate the bio-carbons, including cellulose, various peels, fungal and crustacean chitin, egg white, poplar catkin, lignin, spongin, collagen, and keratin [28,41,46-67]. The term biomass covers all forms of organic materials, including plants either in living and waste form and animal wastes as well as microorganisms, in other words, materials derived from nature. All these biomaterials can be divided into groups (Fig. 7).

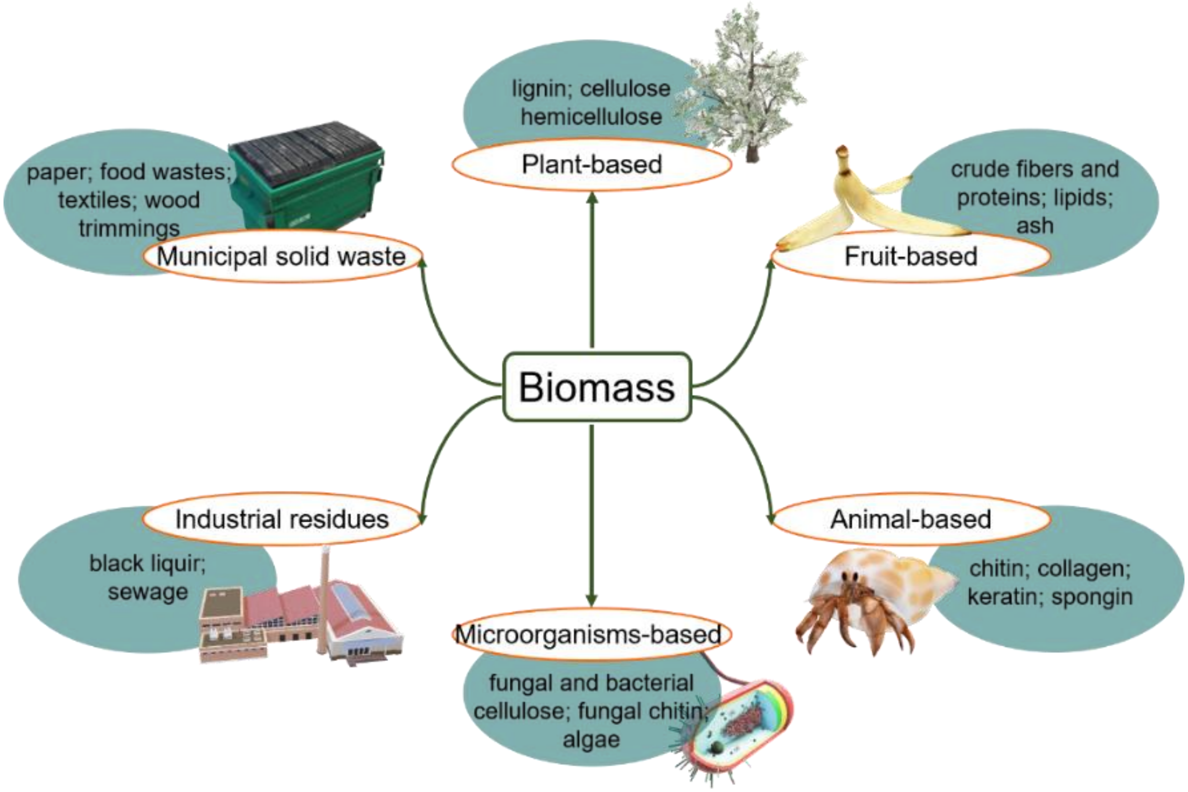


Fig. 7. *Types of biomass, based on* [115].

As presented above, biomass groups differ in chemical and elemental composition, doping level, and structural properties. Consequently, the detailed investigation of the structural-chemical relationship is crucial to find suitable material for the specific application. In Table 3, different types of biomasses are gathered and compared to visualize these differences.

Table 3. *Elemental compositions of different types of biomasses (in dry weight % basis).*

Biomass	**Elemental content (%)**					
	C	**H**	**O**	**N**	**S**	**Ref.**
Coconut coir	46.22	5.44	40.47	0.36	-	[128]
Bagasse	48.60	6.30	45.10	-	-	[128]
Poplar	50.02	6.28	42.17	0.19	0.02	[129]
Corn stover	40.82	5.41	47.85	1.43	0.36	[130]
Rice husk	43.06	0.08	46.60	4.26	-	[131]
Banana peels	35.65	6.19	45.94	1.94	20.75	[132]
Kraft lignin	57.83	3.42	33.66	0.47	4.62	[133]
Rubber seed shell	48.80	5.90	47.30	1.50	0.10	[134]
Saline corn leaves	41.27	5.86	43.86	1.30	0.24	[135]
Chicken feathers	47.40	7.16	n.a	15.12	-	[136]
C. pagurus (crab shell)	43.8	7.20	39.7	6.40	<0.02	[137]
A. bisporus (common mushroom)	42.8	7.10	46.7	3.40	<0.02	[137]
D. confragosa (bracket fungus)	43.30	6.50	50.60	0.20	<0.02	[137]
Spongin	47.00	6.28	n.a	16.06	0.87	[24]
Scenedesmus sp. algae	50.20	6.90	35.80	6.80	0.30	[138]
Collagen from Nukbone®	43.92	n.a	31.41	23.87	n.a	[139]
Collagen protein powder	7.70	n.a	40.30	43.80	n.a	[140]

n.a denotes no information

The importance of the precursors' elemental composition lies in the fact that the oxygen and nitrogen contents can significantly affect the yield, conductivity, and microstructure of corresponding bio-carbons. For example, the precursor's pyrolysis with high oxygen content usually leads to obtaining the bio-carbon with less yield and lower crystallinity, and more defects. On the contrary, the carbonization of nitrogen-rich precursors results in the formation of nitrogen-doped bio-carbons with better electrochemical properties [141,142]. Moreover, the carbonization of carbon-rich sources would not always lead to obtaining bio-carbon with high efficiency. Interestingly, the overall content of carbon is not the main factor affecting the effectiveness of pyrolysis. The presence of thermally stable biomacromolecules with high molecular weight, such as lignin, chitin, and keratin, can ensure a higher yield of aromatic carbon structures [119]. Likewise, doping with sulfur in the form of disulfide bridges is more beneficial among possible sulfur groups. It should be mentioned that not only S-S linkages but other types of intermolecular crosslinking provide the formation of high-quality biomass-derived carbons in high yield [119]. Therefore, to obtain the bio-carbon suitable for catalytic purposes, with a considerably high graphitization order, a low number of lattice defects, and various surface functional groups, the biomass precursor should be nitrogen or sulfur dopped, with possibly low content of oxygen.

Not without significance is the fact that various potential applications of biomass-derived bio-carbons are already gathered in several reviews. For example, Zhou et al. [143] and Deng et al. [144] provided a comprehensive work about the synthesis and application of biomass-derived carbons. Other works focused on bio-carbons particular application, and the mechanism of carbonization was also released [127].

5.3.1. Types of polymorphs and modification procedures of carbonaceous materials

The diversity in the carbonaceous materials is one of the reasons why these solids are attractive for catalysis purposes. However, considering the aspect of catalyst design, knowledge about the polymorphic form of catalysts/support is crucial. As shown in Fig. 8, several different polymorphs of carbon can be differentiated within carbonaceous materials.

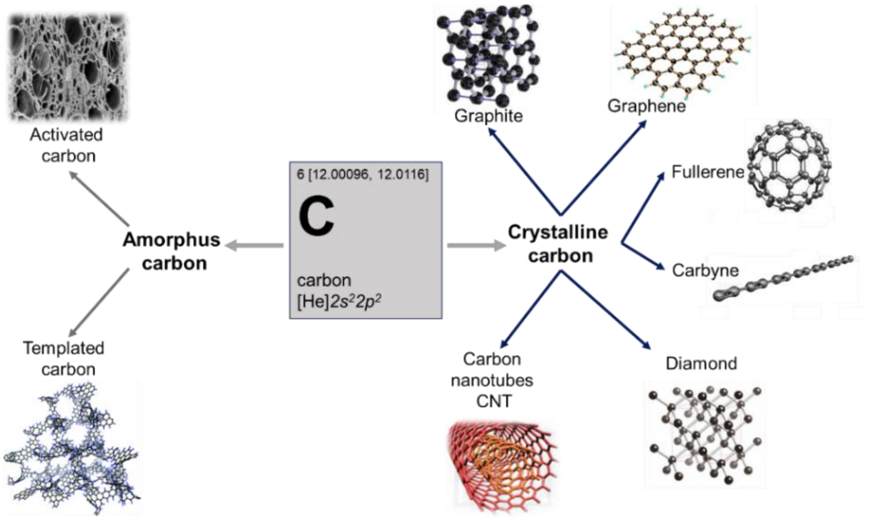


Fig. 8. *Types of carbon polymorphs, based on* [123].

The crystalline polymorphs of carbon are widely utilized in various branches of chemistry, including electrode preparation for energy storage devices, biomedical composites, chromatography, the supports for catalytically active particles, or as catalysts themselves. However, their preparation usually includes the application of high-pressure conditions, harsh and corrosive chemicals. Therefore the accessibility for these materials is somehow limited [145–150].

On the other hand, amorphous carbon is the primary form of carbon built from the disordered graphitic sheets connected by strong covalent bonding in the basal plane. The activated carbon is the most known among the amorphous carbons, and its utilization and production are dated from the XIX century [151]. The vast surface area, micro-, and mesopores, with a significant volume and controlled geometry, are the main reason for applying activated carbon in heterogeneous catalysis, among others [152,153]. Interestingly, practically every carbon material, which constitutes a significant carbon source, can be evaluated as a potential activated carbon source [121,152,153]. For example, due to their easily tuned surface functionality, porosity, and large surface functional groups, bio-carbons are considered activated carbons.

Nevertheless, the preparation of activated carbons involves several steps, including the pre-carbonization at moderate temperatures (up to 800 °C), followed by chemical or physical activation and final carbonization. The activation step often requires the application of various toxic chemicals and results in a significant amount of waste. Due to these disadvantages, another polymorph of amorphous carbon – the templated carbon was developed [127,154,155].

The advantage of templated carbons is the possibility of designing and controlling the shape and size of pores and overall structure. Their synthesis is mainly based on the soft- and hard-template approaches. As a result, materials with a high surface area (up to 4100 m^2/g) with huge pore volume can be obtained [156,157]. However, it must be mentioned that the preparation of carbonaceous materials with strictly desired structure, geometry, and porosity might be achieved by applying the proper source of carbon – for example, biomass [116,117,158–160]. The natural precursors offer a wide variety of structures, geometries, and chemical compositions.

Moreover, the carbonization using the inner gas atmosphere results in preserving the structure of resulted templated carbon and develops the nanoporous structure *in-situ* [119,127,158]. The fabrication method based on simple carbonization and sometimes additional activation processes do not need high-pressure systems and harsh chemicals. Although, the proper biomass source selection is a critical point in the development of structural carbons. The chemical composition and the presence of various heteroatoms influence the yield of carbon product, porosity, and final chemical composition. Therefore, the chemical-structure relationship is essential to find a proper precursor for desired application [119,125,127]. Nonetheless, the price of biomass precursor and the cost and efficiency of manufacturing still has a decisive influence on the precursor choice. Some biomaterials, such as the eggshells or silk cocoon, despite their superior properties after carbonization, are excluded from commercial use due to the necessity of carbonizing the significant amount of precursors [114,161,162].

The methods of structured carbons functionalization have been developing based on the resulting product's already desired application. Generally, surface functionalization is carried out using *in-situ* or post-synthetic approaches to implement different chemical moieties, which are essential for various applications – including catalysis. The general strategy of carbonized materials modification, including the structured one, is shown in Fig. 9.

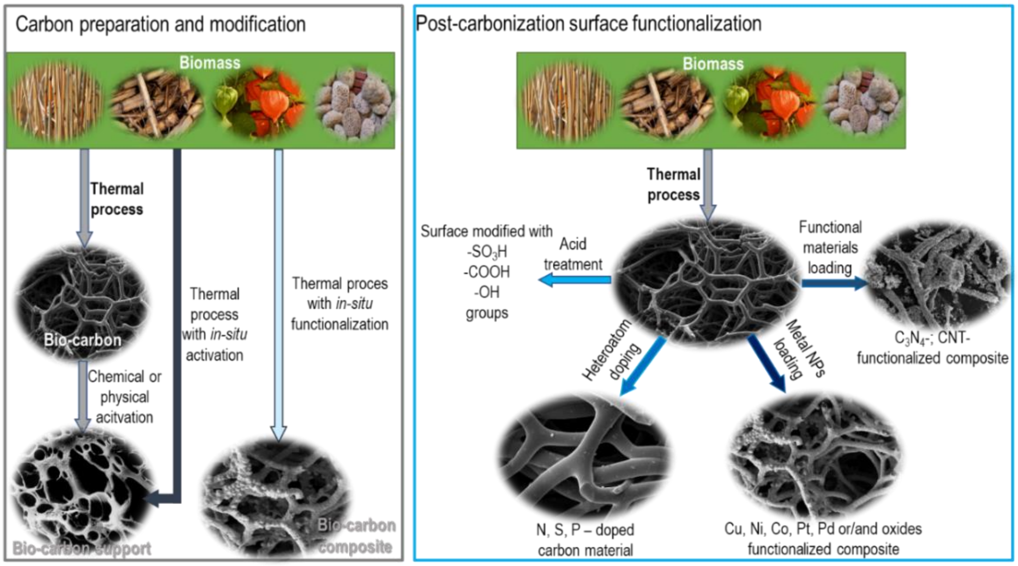


Fig. 9. *The general strategy for the bio-carbons preparation and structure functionalization, based on* [125].

One of the most standard functionalization methods is acid modification through introducing the sulfonic groups using concentrated sulfuric acid or its derivatives [163].

The sulfonic groups are the standard class of Brønsted acid and, together with hydroxyl and carboxyl groups, enhance the catalytic activity of biocarbon, especially in esterification and hydrolysis reactions [164].

The functionalization of carbonaceous material with metal particles can be carried out either after carbonization or *in-situ* during thermal treatment. Usually, the treatment of carbonaceous matrix after carbonization is related to the soaking of carbon solid in the solution of metal salt. The ions of metal enrich the pores and surface of the treated material. The thermochemical or chemical processes are implemented in the next step to obtain the metal oxide on the carbonaceous material's surface [165,166]. The impregnation-precipitation procedure can also be carried out by mixing two agents, where the metal-carrying reagent is also precipitant. Sometimes, the hydrolyzing agents are used to enhance the precipitation of metallic particles.

On the other hand, the impregnation of carbon precursor with metal salts prior to carbonization results in carbon-supported metallic composite *in-situ* [167]. In this case, the metallic precursor is not only adsorbed on the surface of the precursor but also gets into the precursor interior. Then, during the thermal treatment in an inert atmosphere, it can form a metallic phase. Similarly, magnetic particles can be introduced to the carbonaceous material [168]. Unfortunately, all the different types of impregnation, impregnation-precipitation, or sorption-reduction methods suffer some disadvantages, mainly the poor particle dispersion and blocking of active sites [125]. The introduction of carbon surface functionalization via heteroatoms doping, surface grafting, or oxygen groups is applied to overcome these obstacles [147,169,170]. The wide variety of surface functional groups on the carbonaceous surface creates more attaching sites, enhances the sorption efficiency, and improves the metallic particle dispersion [147]. Moreover, functional crystalline carbon polymorphs like graphene, graphene oxide, carbon nitride, carbon nanotubes, and zero-valent iron can also successfully modify the structure of carbonized material, combining the superior properties of two components – structured carbon and the crystalline carbon polymorph [121,165].

On the other hand, biomass utilization for bio-carbons production is also advocated from the kinetics point of view. The knowledge of the value of activation kinetics is a crucial factor in selecting the biomass precursor. Considering the literature report, the values of activation energies calculated using either model-involved and model-free methods for lignocellulosic materials do not exceed 300 kJ/mol [171–173]. Interestingly, proteins are characterized by significantly higher values of activation energies being in the range of 80 kJ/mol, even up to 1000 kJ/mol [174–176].

Considering the possibilities mentioned above of bio-carbons preparation and their final physicochemical properties, their use in heterogeneous catalysis seems to be justified. Therefore, the main directions of using bio-carbons as metal phase support or structured catalysts are discussed in the next part of the dissertation.

5.3.2. Application of structured bio-carbons in catalysis

The structured bio-carbons have indeed gained significant attention, not only because of the incredible variety of precursors, which can be inexpensive and renewable [119,144,148,177]. The properties of resulted materials including low density, diverse porous structure, easy accessibility, low cost, resistance to primary and acidic media, good resistance for hydrolytic effect in an aqueous environment, recycling ability, and above all possibility to functionalize the surface by activation, impregnation of doping methods, make them promising catalysts supports and even catalytically active materials [165,167]. Their utilization as potential catalytic materials is related to the presence of various heteroatom doping, high surface area, and the defects and holes in the crystalline structure that can act as active sites [116]. The designed hierarchical structure provides good diffusion and accessibility parameters during catalytic processes [178]. The possibility for applying carbonaceous materials as sorbent and catalysts was first shown by Robert W. Coughlin in 1969 [179]. Coughlin explained the behaviour of carbonaceous materials from the structural, electronic, and surface chemistry point of view and explained their catalytic activity due to their physicochemical properties, including surface chemistry, crystalline structure, and existence impurities. This work was a starting point for further developing of carbonaceous structures in catalytical application [180,181]. The carbonaceous materials are currently investigated under the name carbocatalysts or metal-free catalysts in different reactions. The 4-nitrophenol reduction is a well-recognized reaction that occurs using the carbonaceous materials (dopped or not) as a catalyst [182,183]. Also, other oxidation and photooxidation reactions or even C-C bond formation reactions can be catalyzed with carbonaceous materials [121,145,182].

On the other hand, the use of metal-free catalysts is still limited only to the laboratory scale. This is related to the expensive doping processes, high fabrication costs of crystalline carbons, or the insufficient stability of carbonaceous materials obtained from the biomass. Therefore, analogous to mesoporous silica or zeolites, the structured carbons can be transformed into the next level of applicability by their surface functionalization with various molecules. Such transformation leads to further optimizing the interfacial and bulk properties of catalysts and can open the way to develop new advanced applications [156,165,184].

At the same time, carbonaceous materials have been used as a support for metallic as well as metal derivatives particles. Surprisingly, for the first time in 1984, the methodology of dispersion of metal or metal derivatives particles on carbonaceous substrates was described [185]. From this time, the various carbon-based composites have been widely utilized in different catalytic reactions – as is shown in Fig. 10.

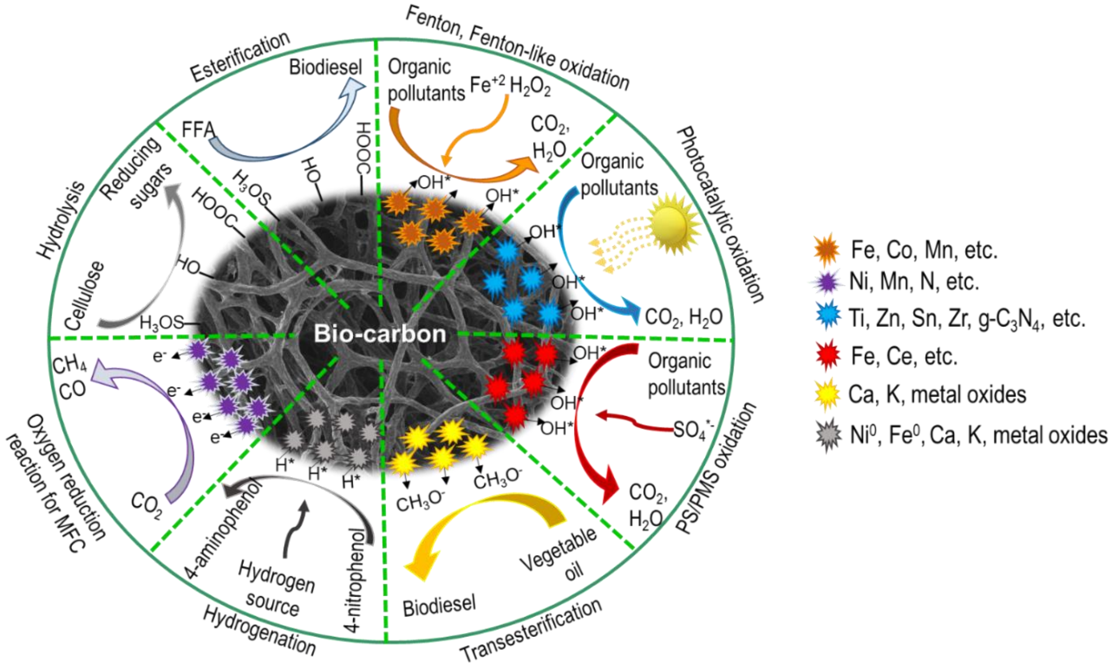


__Fig. 10.__ The catalytic application of bio-carbon-based materials, based on [125].

Within the tremendous amount of catalytic reactions, the advanced oxidation processes (AOPs) can be considered one of the most crucial processes developed nowadays [186]. These considerably low-costs processes required using catalysts and oxidants, mainly hydrogen peroxide, to synthesize the hydroxyl radicals responsible for the decomposition of organic pollutants [187]. Various modification of the general idea of this oxidation proves have evolved. In photocatalytic processes, the presence of an oxidant is often replaced by UV light, or it synergistically interacts with the oxidant and photocatalysts. The latter is usually composed of titanium, zinc, zirconium, or oxides [188–191]. However, historically the first oxidation process was carried out by Henry John H. Fenton, who used a small number of ferrous ions to oxidize the tartaric acid with hydrogen peroxide.

In conclusion, Fenton proved that the Fe^{2+} takes part in the reaction as a catalyst, with a minimal amount being enough to promote the complete degradation of even a considerable volume of tartaric acid [192]. Since then, homogeneous and heterogeneous Fenton-oxidation processes have been developing using various catalysts, including iron, cobalt, or manganese-based composites [181,187]. On the other hand, more attention has been paid to sulfate radical-based oxidation processes (PMS) [190] in the last decade. In this eco-friendly approach, the sulfate radicals are generated by activating peroxymonosulfate (PMS, HSO_5^-) [193]. To date, various catalysts based on cerium, iron, or cobalt have been evaluated in this process [194–198]. It must be mentioned that, recently, carbonaceous materials have been recognized to be promising supports for catalytically active phases and catalysts on their own [199]. The immobilization of metal-containing phase on the surface of carbonaceous materials is a reasonable pathway, considering their low cost. In contrast, carbonaceous materials are derived from biomass, unique electrical properties, renewability, rich surface chemistry. Therefore the bio-carbon together with the bio-carbon-based composited have gained much attention [125].

Another critical group of catalytic reactions, which has long been in industrial and academic interest, is the hydrogenation reactions [125]. In these reactions, different industrially important nitroarenes are produced, which are further used to produce pharmaceutically active compounds, agrochemicals, dyes, fine chemicals, and polymers. Moreover, the hydrogenation of nitroaromatics often gives intermediary compounds such as hydrazines, hydroxylamines, azoarenes, and azoxyarenes [200–204]. In those processes, the catalysts are prepared mostly from precious metals such as Pt, Pd, Rh, Ir, or Au. However, their high price and limited ability result in looking for cheaper alternatives. Currently, zero-valent nickel or its oxides, as well as zero-valent iron or nickel-molybdenum composites, are widely applied. However, single-component catalysts are characterized by low effectivity, selectivity, and stability and often require high-pressure processes and high temperatures [203]. Because good surface exposition is a key point to obtain high catalytic activity and being aware of a negative agglomeration effect that hampers the stability and activity of nanoparticles led to the formation of structured, supported catalysts. For this sake, bio-carbons with a well-developed hierarchical structure are promising candidates. The utilization of such bio-carbon-based catalysts is a prominent pathway in developing catalysts for nitroarenes hydrogenation nowadays [200,203]. Not without significance is the fact that hydrogenation of lignin and furfural or production of n-heptane are also one of the most evaluated reactions where the bio-carbons and their composited are tested [205,206]. The proper development of the metal-containing phase plays an essential role in creating the electron reservoir during the reduction. Moreover, the structure of carbonaceous support must guarantee the proper diffusion and minimalization of deactivation phenomena. Therefore, currently, the naturally structured bio-carbons support is developed.

It is well known that the acid catalysts can be applied to the esterification and transesterification reactions [207,208]. In esterification reaction, the biodiesel is synthesized from inexpensive feedstock with high content of fatty acids (FFA), including non-edible vegetable oil waste and cooking oils, among others. Only in the last decade application of bio-carbons derived from biomass as a simple catalyst for esterification reaction has been evaluated. The biomass precursor is usually carbonized in a lower temperature in the range of 400-600°C, functionalized with a sulfonic group that can be successfully applied as a carbocatalyst in the esterification of acid oil. Compared to standard solid acid catalysts, the favorable catalytic activity of functionalized bio-carbons, including the HZSM-5, is related to the strong acidic sites of functionalized carbocatalysts [209,210]. The straightforward procedure of preparation followed by a simple functionalization procedure is the main advantage of bio-carbons over the solid commercial catalysts in this type of reaction [207]. Nevertheless, the challenge to find more effective ways to perform the esterification and transesterification reactions is still open [164,211,212].

The bio-carbon-based catalysts can also be applied for oxygen reduction reactions (ORRs) in microbial fuel cells (MFC). In the last decade, a considerable number of studies have been published on this topic. For instance, the sewage sludge has been described as naturally rich in nitrogen and other transition metals feedstock of self-supported bio-carbon [213]. High pyrolysis temperature led to obtaining bio-carbon rich in heteroatoms which exhibited high activity in the oxygen reduction reaction. Within the years of research, it was proved that the existence of heteroatoms including S and N have a positive effect on the ORR efficiency by changing the electronic structure of bio-carbons. Within the time, various carbocatalysts and bio-carbons functionalized with metal-containing phase derived from watermelon rind, waste pomelo peels, corncob Enteromorpha, among others, have been prepared and successfully utilized as electrocatalysts in ORRs [214–217].

The utilization of catalysts based on biocarbons in catalytic conversion of biomass is also an important point to evaluate. Great attention has been paid to the degradation of non-edible parts of biomass such as cellulose, lignin, among others [218,219]. Various inorganic oxides deposited on carbonaceous supports have been evaluated as potential catalysts, such as cellulose conversion to sugar alcohols. Such materials show promising activity due to their ability to selectively position catalytic metals, water tolerance, and tailorable surface area, enhancing catalytic dispersion [218,220,221]. Moreover, compared to classic zeolite-based catalysts, the carbon-based materials show better selectivity toward the formation of sugar alcohols and better resistance to hydration. Moreover, the constant development of 3D carbon materials with versatile and accessible pore structure increase carbon role as a support for biomass conversion [222].

It is visible that bio-carbons represent one of the most industrially and technologically promising materials because of their relatively easy synthesis, low costs, and the tremendous number of composition/synthesis possibilities. Additionally, bio-carbon-based catalysts have been recognized as decently designed by well-developed methodologies utilizing high surface area, porosity, and rich surface chemistry. Nevertheless, their application in catalysis is still limited due to several challenges. Mainly their complex surface chemistry and heterogeneity impede the tailoring of the catalyst surface on a multi-level stage. Therefore, the development of several approaches in the design and synthesis of bio-based catalysts is observed. Firstly, it is crucial for future research to prepare low-cost catalysts based on bio-carbons and cheaper metals instead of noble or rare metals and the enhancement of recovery and recycling of materials. The catalyst design procedure should also include large-scale manufacturing capabilities. Secondly, the proper identification of functionality, catalytic activity, and the synergy effect of metal-containing phase with the bio-carbon, the understanding of the mechanism of action of resulted catalysts might open a door for finding a new branch of utilization in industrial catalysis.

Furthermore, finally the type of biomass that determines the properties of resulted bio-carbon. The future study must combine the properties of biomass feedstock with the mechanism of catalyst reaction to extend the scope of application. Moreover, the selection of bio-carbon precursor must be based on its accessibility, renewability, and proper structure to obtain the desired bio-carbon via facile, low-cost, and straightforward preparation procedure.

Owing to mind the above discussion, a general conclusion has been drawn. Spongin is a promising source of material that can be used to produce structured bio-carbon using the biomimetic approach. The unique mechanical stability and chemistry give endless opportunities for molding the final properties of the prepared composite. In the presented PhD dissertation, the detailed description of the carbonization process is shown in detail (**Publication 4**) by means of a description of the kinetics of this process. Furthermore, the evaluation of low-temperature carbonization to obtain the functional support for the metal-containing phase was described for the first time in **Publications 5 and 6**. A thought description and motivation for the following works are presented in chapter 5 of the dissertation.

6. DESCRIPTION OF THE CONTENT OF PUBLICATIONS

The results presented in **Publications 1-2** contain a detailed investigation regarding the isolation and identification of chitin in sponges of various orders. It must be mentioned that since the first discovery of chitin in the skeleton of marine sponges, the studies focusing on monitoring of other species among representatives of four classes of sponges (Hexactinellida; Calcarea; Demospongiae: Homoscleromorpha) are continued.

The particular interest in seeking new sources of chitin-based scaffolds of sponge origin is connected to the fact that those scaffolds resemble the shape of the sponge skeleton. In other words, the isolation of chitin from sponges results in the formation of ready-to-use, unique, and naturally pre-structured scaffolds. Consequently, in **Publication 1**, chitin has been discovered in demosponge *Pseudoceratina purpurea* (Carter, 1885) representative of genus Pseudoceratina within Verongiida order, collected in the coastal waters of Singapore. This work describes the first attempt to extract and identify chitin from a member of the Pseudoceratina genus.

In **Publication 2**, the representative of Poecilosclerida order: *Mycale euplectellioides* (Heteroscleromorpha: Poecilosclerida: Mycalidae) collected in the Red Sea was investigated as a new source of chitinous scaffolds. Similarly, a detailed study of the isolation and identification of chitin from the skeleton of representative of this order was shown for the first time.

Both studies' approach for chitin isolation is based on the stepwise extraction as shown in Fig. 11, which led to obtaining spicule- and protein-free 3D scaffolds (see Fig. 12).

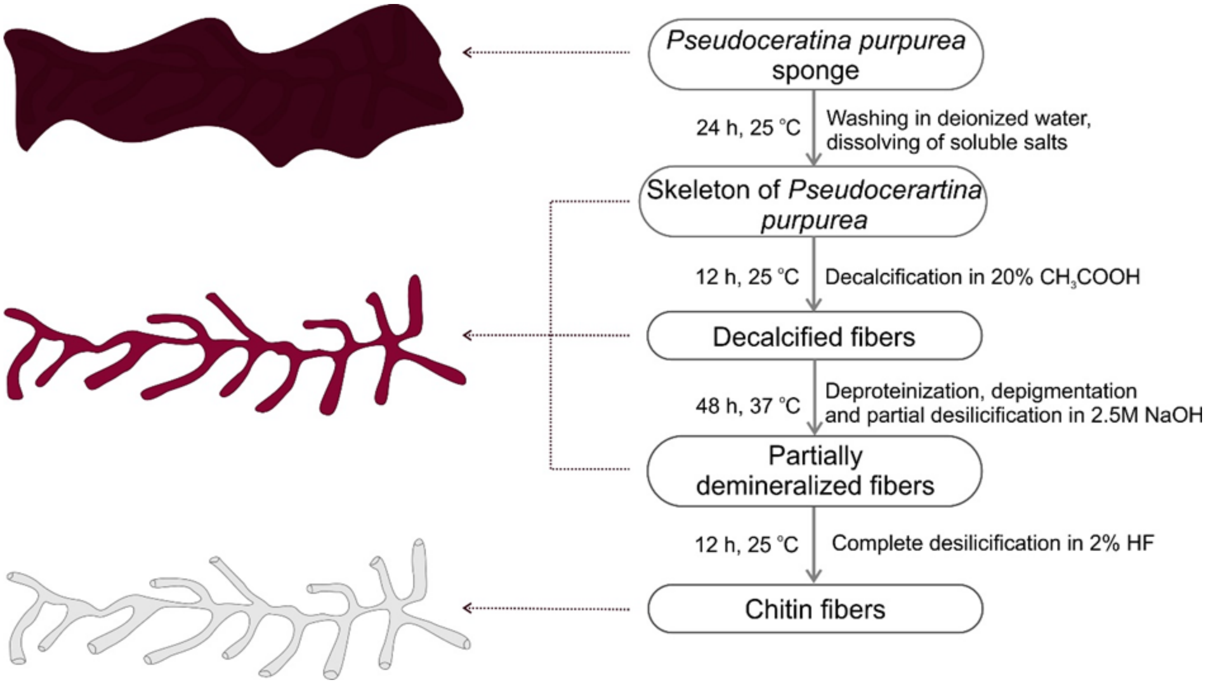


Fig. 11. *Step-by-step isolation procedure of chitinous scaffolds from the skeleton of marine demosponge P. purpurea (**Publication 1**).*

Depending on the sponge species, after decalcification and deproteinization processes, additional desilicification is needed to remove existing siliceous spicules or sand particles. For this reason, desilicification is carried out using a diluted solution of hydrofluoric acid. Moreover, the sodium hydroxide and acetic acid concentrations are far below the threshold concentration where the transformation of β-chitin into α-chitin starts to occur.

Thus, the applied conditions do not destroy the 3D structure of isolated chitin. At this point, it should be mentioned that the influence of acidic and alkali treatment was thoughtfully investigated using stereo and fluorescence microscopy.

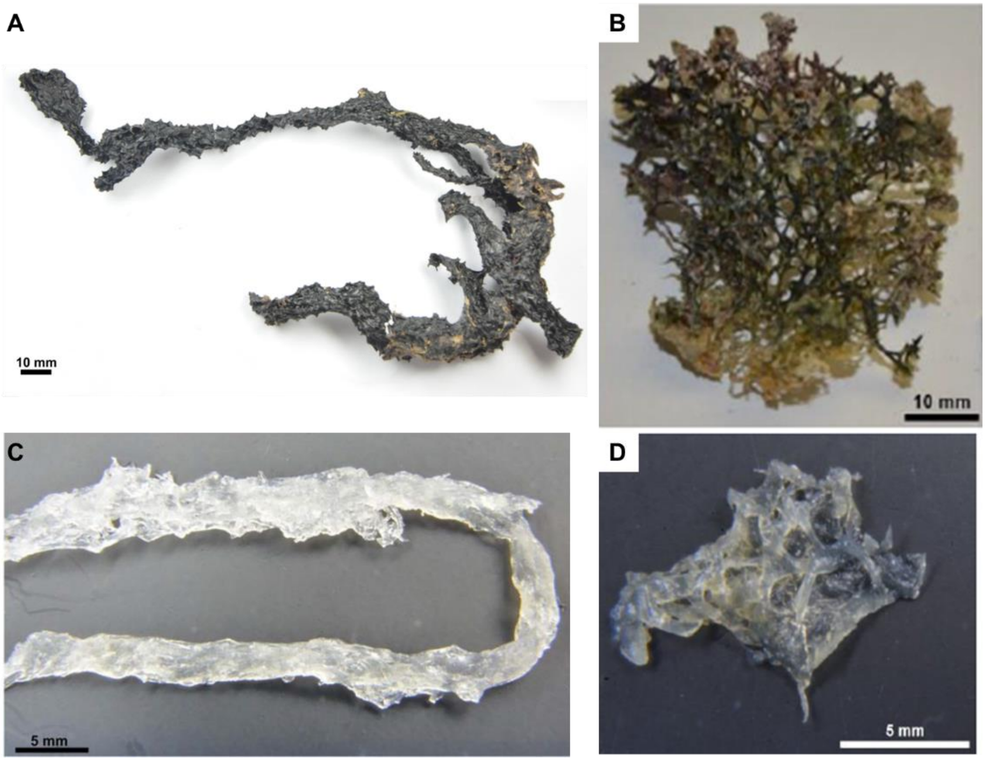


Fig. 12. *Fragment of a freeze-dried specimen of P. purpurea (A) and M. euplectelloides (B) demosponges with their completely pigment-free and demineralized scaffold isolated using the approach described in* ***Publications 1 and 2****.*

The microscopic study proved that the applied chemical treatment does not destroy the structure of isolated chitinous scaffolds (Fig. 12B, D). Still, it led to obtaining a three-dimensional tubular scaffold with translucent structure and exhibiting micro- and nanofibril organization (for comparison, see SEM images in **Publications 1 and 2**). Both obtained chitinous scaffolds closely resembled the morphology of sponge. Likewise, the investigation proved that the additional treatment with diluted hydrofluoric acid is essential to obtain pure organic microfibers and complete removal of foreign spicules and other debris. Interestingly, such treatment does not destroy the fragile structure of isolated chitinous scaffolds, even after the dissolution of supporting spicules (please see the optical and SEM microscope images in **Publications 1 and 2**), as well as does not lead to obtain chitosan.

At this point, it should be mentioned the primary difference between the isolated scaffolds from *P. purpurea* and M. *euplectellioides*, the microfibers of the latter are not densely packed as in the case of multilayered microfibers observed in various representatives of verongiid sponges – and *P. purpurea*.

After successful isolation (Fig. 12), the identification of chitin was carried out using various bioanalytical tools. Calcofluor white staining, Fourier-transform infrared spectroscopy (FTIR), electrospray ionization mass spectrometry (ESI-MS), and fluorescence microscopy, as well as a chitinase digestion assay, were applied to confirm with strong evidence the finding of α-chitin in the skeleton of either *P. purpurea* or *M. euplectelloides.*

The calcofluor white staining (CFW) is the first step for the preliminary recognition of the presence of chitin in isolated skeletons. The fluorescent dye binds to the particular bonds in β(1→3) and β(1→4)-linked polysaccharides, and as a result, emits a bright blue light under UV excitation [47]. By using fluorescence microscopy, the changes after staining can be observed. Such observations for stained chitinous scaffolds isolated from *P. purpurea* and *M. euplectellioides* showed strong fluorescence even under light exposure time as short as 1/3700 s.

Further confirmation of the chitinous nature of isolated scaffolds focused on evaluating the course of enzymatic and acid hydrolysis. Subsequently, the enzymatic digestion tests were carried out using the chitinase enzyme, as was previously performed during the isolation of chitin in various sponges. The chitinase enzyme can degrade chitin into low molecular oligomers (such as N-acetylglucosamine (GlcNAc)). The degradation process can be monitored using an optical microscope, as is shown in **Publications 1 and 2**. Such a test is additional confirmation of the chitinous nature of isolated scaffolds. Furthermore, the Morgan-Elson assay has been applied to determine the amount of D-glucosamine released after chitinase tests. Accordingly, the 950 ± 1.5 µg and 700 ± 1.5 µg of N-acetylglucosamine per mg of the isolated chitinous scaffold was released. Such results are in accordance with that reported for chitin isolated from other demosponges.

In addition, the electrospray-ionization mass spectrometry technique was applied to confirm the presence of chitin. Consequently, the acid hydrolysis of chitin was carried out, resulting in the formation of D-glucosamine, which is easily detected using the ESI-MS method

(Fig. 13). Such an approach is a standard procedure applied for the identification of chitin, even in complex organisms.

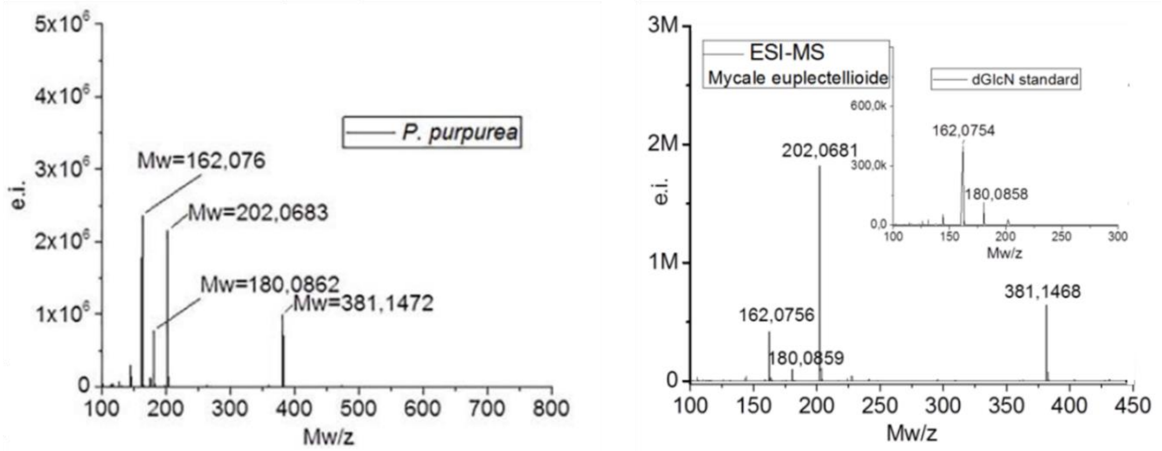


Fig. 13. *The ESI-MS spectrum of chitin isolated from P. purpurea and M. euplectelloides with spectra of commercial D-glucosamine (as inner plot).*

The spectra of both *P. purpurea and M. euplectelloides* show the same ion peaks. The ion peak of *m/z* 162 and 180 are identical to the peaks of the standard D-glucosamine spectrum. The ion peak *m/z* 162 is equivalent to the D-glucosamine molecule after losing the H_2O molecule, and ion peak *m/z* 180 is related to the $[M+H]^+$ molecule of D-glucosamine. The additional ion peaks *m/z* 202 and *m/z* 381 are connected to species paired with K^+ accordingly $[M+K]^+$ and $[2M+K]^+$, which the latter is a non-covalent dimer.

On the other hand, more sensitive techniques were also used to identify the chitin within the isolated scaffolds. For this reason, FTIR and Raman spectroscopies were applied. Both methods are liable for intra- and intermolecular interactions and geometry of the molecules. Thus, the isomorphic type of chitin can be distinguished. In Fig. 14, the FTIR spectra of chitin isolated from *P. purpurea* and *M. euplectelloides* are shown compared to standard α-chitin. The results of Raman spectroscopy analysis are demonstrated in **Publication 1**.

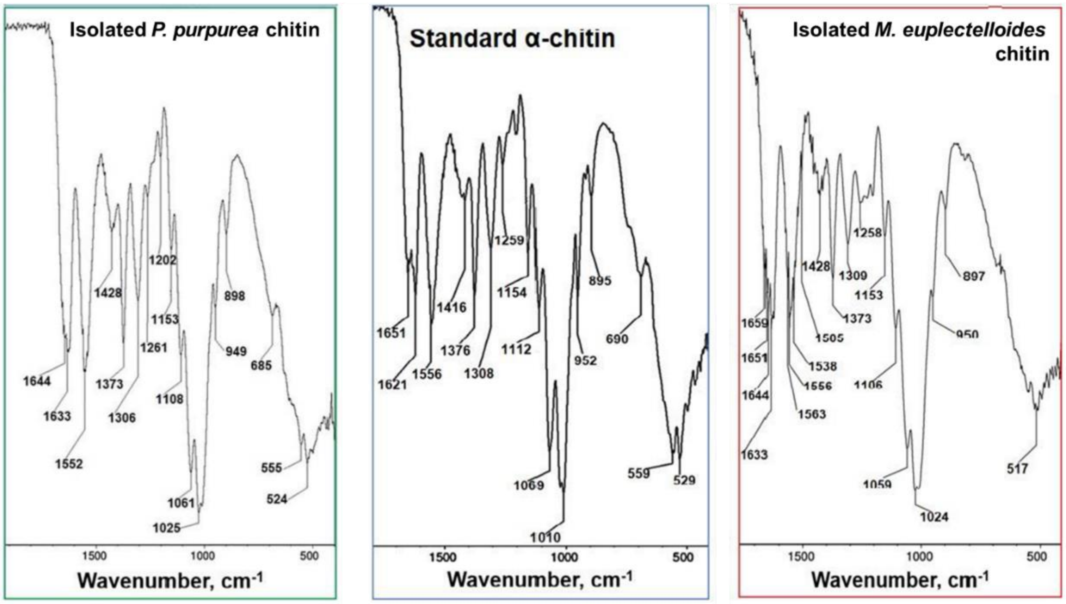


Fig. 14. *The 1700-500 cm^{-1} region of FTIR spectra of chitin isolated from P. purpurea and M. euplectelloides compared with spectra of standard α-chitin.*

The amide moiety region between 1700-1500 cm^{-1} is essential to differentiate the proper chitin polymorph. In this region, either the spectra of chitin isolated from *P. purpurea* or *M. euplectelloides* show an intense amide band I assigned to stretching vibrations of C=O groups. The characteristic feature visible for α-chitin is splitting the amide I band into two subpeaks due to intermolecular C=O N-H and C=O HO-CH_2 hydrogen bonds. Such feature is depicted on spectra of chitin from *P. purpurea* and *M. euplectelloides.* Likewise, the band at wavenumber 949 cm^{-1} for *P. purpurea* chitin and 950 cm^{-1} for *M. euplectelloides* chitin is characteristic of CH_3 wagging along chain vibrations, and it is typical for α-chitin.

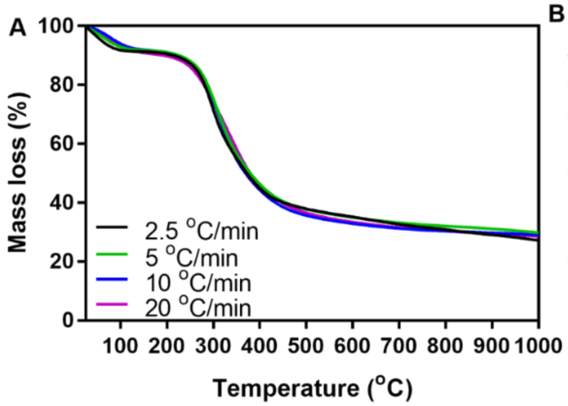
Furthermore, the very indicative band assigned to β-glycosidic bonds is observed at a wavenumber of 898 cm^{-1} and 897 cm^{-1} for *P. purpurea M. euplectelloides* chitin, respectively. The detailed comparison of measured spectra with the one from α-chitin shows the strong resemblance of chitin polymorph. Moreover, the obtained spectra do not exhibit the bands characteristic for $CaCO_3$ (855-867 cm^{-1}) and SiO_2 (720 cm^{-1}), which confirms the purity of isolated chitinous scaffolds.

The importance of the above-described works lies in the fact that the discovery of chitin within the representatives of Pseudoceratina, and the Mycale genus, is a critical step in evaluating these globally distributed sponges as a new source of chitin and possibly biologically active compounds that are promising to be used in biomedicine and pharmacology, respectively. As it was stated in **Publications 1 and 2,** both sponges are, probably, among the richest sources of pharmacologically active compounds such as pateamines [223], mycalolides [224], purealidins [225], aplysamine [226-227], among others. All those compounds exhibit promising properties to produce novel drugs and other pharmacologically active molecules. However, the biggest challenge, so far, is related to develop the technique of subsequent isolation of chitinous scaffolds and those metabolites.

Spongin was another biomaterial of sponge origin evaluated according to the second pathway of biopolymers utilization explored within the framework of this thesis. Spongin-based skeletons' usefulness as a source of structured bio-carbons was studied in detail in **Publication 3**. In this work, for the first time, the thermal decomposition behavior of spongin-based scaffolds isolated from *Hippospongia communis* marine demosponge was characterized by using thermogravimetric analysis. Additionally, the study of volatile products released during thermal treatment was performed using mass spectrometry.

Evaluating the kinetics of thermal degradation of any biomaterial is essential from the process design point of view. Knowing the course of thermal degradation helps determine the optimal pyrolysis condition and finally obtaining the product with strictly designed properties. Consequently, the description of that aspect for such promising biomaterial as spongin is fundamental and constitutes the innovative element of the mentioned work.

Thus, the thermogravimetric analysis of spongin-based scaffolds was performed in the first stage with the different heating rates (Fig. 15A).



B

Possible assignment	Characteristic peaks (m/z)	Peak temperatures (°C)
H_2O	16, 17, 18	100, 300 °C
CO_2	12, 16, 22, 28, 29, 44, 45, 46	200, 340, 600, 800 °C
C_2H_2	25, 26	200–700 °C
C_3H_6	27,39,40, 41, 42	200–700 °C
$(CH3)_2CO$	43	200–500 °C
NH_3	15,16,17	250–700 °C
NO	15, 16, 30	200–500 °C
NO_2	16, 30, 46	600–950 °C
HCN	26, 27	250–600 °C
CH_3CN	39, 40, 41	280–500 °C
H_2S	33, 34	250–450 °C
SO_2	48, 64	270, 890–1000 °C
$(CH_3CO)_2S$	43	200–500 °C

Fig. 15. *TG curves of spongin-based scaffolds measured in the temperature range 25-1100 °C (A) with the possible product degradation identified by MS during thermal treatment spongin scaffold in an inert atmosphere (B).*

In **Publication 3**, it was indicated that the heating rate does not influence the thermal degradation course. Typical two-weight losses, described in other words, are observed. First, noted at temperature range 80-150 °C is a consequence of evaporation of humidity and physically adsorbed water. The second significant mass loss is observed at temperatures between 200-420 °C, and it can be associated with the thermal decomposition of peptide bonds, disulfide bridges, and breaking of hydrogen bonds. In addition, this negligible weight loss observed at higher temperatures might be a consequence of the different heating rates applied, which affect the kinetics of material transformation. Besides, the results of TG-QMS analysis (Fig. 15B) proved that various gases such as H_2O, CO_2, NH_3, NO_x, HCN, SO_2, H_2S, hydrocarbons are released together with the thermal treatment. The temperature of releasing the sulfur or nitrogen can be estimated, which is essential to design the carbon-based material dopped with a particular heteroatom. Moreover, those results showed that the degradation products are also released at temperatures as high as 600-950 °C. Additional, low-temperature nitrogen sorption tests performed from material obtained after pyrolysis in different temperatures (for comparison, see **Publication 3**) proved that with the increase of pyrolysis temperature, the surface area of resulted material also increases, and pore volume and size of pores decrease.

However, the most important part of **Publication 3** was calculating the kinetics of spongin thermal degradation. The kinetic parameters: activation energy E_A, pre-exponential factor A and analytical form of reaction model function $f(\alpha)$ and $g(\alpha)$ were calculated using the methods including integral Coats-Redfern approach, where the 17 solid-state kinetics models were checked to express the dependence of conversion on the process rate. Likewise, model-free iso-conversional methods based on the assumption that the reaction rate is only a function of temperature for a given constant value of the extent of conversion were also used to calculate kinetic parameters.

$$r = \frac{d(m_\alpha - m_f)}{dt} = k(T) f\left(m_\alpha - m_f\right), \tag{1}$$

$$k(T) = A exp\left(\frac{-E_A}{RT}\right), \tag{2}$$

where t denotes time (min), α is the degree of conversion, $f(m_\alpha - m_f)$ is the kinetic part of the equation related to the mass of reactant taking part in the reaction, m_α and m_f are the masses of the sample measured for a specified α, and in the final stage respectively, $k(T)$ is the kinetic rate constant, A (min^{-1}) is the pre-exponential factor, E_A (kJ/mol) is the activation energy, T is the absolute temperature, and R is the universal gas constant (8.314 J/mol·K). Consequently, using the $k(T)$ from equation (2), linking dt to the heating rate into, and rearranging the equation (1) can be written as:

$$\int_{\alpha_0}^{\alpha} \frac{d\alpha}{f(\alpha)} = \int_{T_0}^{T} A\, exp\left(\frac{-E_A}{RT}\right)\frac{dT}{\beta} = g(\alpha). \quad (3)$$

As a result, equation (3) is used as a starting equation to evaluate thermal degradation kinetics. In Table 4, the final linear equations obtained using various methods are given.

Table 4. *The numerical method applied to calculate the kinetics of thermal degradation of spongin-based scaffolds.*

Calculation method	Final equation
Integral Coats-Redfern	$\ln\left(\frac{g(\alpha)}{T^2}\right) = \ln\left(\frac{A\,R}{\beta E_A}\right) - \frac{E_A}{RT}$
Model-free iso-conversional Friedman	$\frac{d\alpha}{dt} = \ln\left(Af(\alpha)\right) - \left(\frac{-E_A}{RT}\right)$
Model-free iso-conversional Kissinger-Akahira-Sunose (KAS)	$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{A\,E_A}{R}\right) - \frac{E_A}{RT}$
Model-free iso-conversional Ozawa–Flynn–Wall (OFW)	$\ln(\beta) = \ln\left(\frac{A\,E_A}{R}\right) - 2.135 - 0.457\frac{E_A}{RT}$

Where: f(α) and g(α) are model functions.

Furthermore, based on the kinetic calculations, the changes of entropy (ΔS), enthalpy (ΔH), and free Gibb's energy (ΔG) were evaluated using the theory of the active complex of the reagent.

Before kinetics calculations, the course of the reaction profiles was plotted for each value of heating rate as a function of the degree of conversion versus reaction time. Based on that, three reaction stages could be distinguished (for comparison, see Fig. 4 in **Publication 3**). The first stage can be associated with the decomposition of some impurities and the desorption of absorbed water. This part is omitted from the overall kinetic calculation due to its physical nature. The primary pyrolysis process begins when the degree of conversion (α) is higher than 0.11 and decomposition progressively increases; thus, the highest rate is achieved, and this part is called the acceleration period. Finally, the declaration period begins when the process rate slowly decreases and lasts until the reaction is completed.

Consequently, based on the data obtained from TG, the calculations of kinetics were performed. The calculated values of activation energies using the Coats-Redfern approach were in the range of 39.3–48.7 kJ/mol. The best correlation of experimental data with theoretical models was achieved for the third-order reaction model. Thus, it was assumed that this model could be used to describe the mechanism of thermal degradation with the highest accuracy. On the other hand, within the Coats-Redfern approach, a good correlation of experimental data with theoretical models was also achieved for diffusion model type 4 – Zhuravlev equation with calculated activation energies in the range 64.2–81.5 kJ/mol. Nevertheless, due to the nature of spongin-based scaffolds, it was suggested that diffusion would not have a decisive impact on the overall rate of pyrolysis.

Interestingly, the calculated values of activation energies were significantly higher for model-free iso-conversional methods than data obtained using the Coats-Redfern approach. Such results are connected to the different approximations of temperature integral used in each proposed method. Not without significance is the fact that the correlation coefficients calculated for model-free iso-conversional methods are lower than for the Coats-Redfern approach. It is apparent especially for the Friedman model, where the low correlation coefficient obtained for calculations with those results was excluded from evaluation. Consequently, due to low values of correlation coefficients, it seems that the iso-conversional methods cannot describe the thermal degradation of sponging with excellent approximation.

As mentioned before, the topic discussed in **Publication 3** is fundamental from the design point of view. The knowledge of activation energy value can help choose the proper biomass precursor for the production of novel bio-carbons. Moreover, bringing together those results with the evaluation of the properties of received biocarbons will give a comprehensive overview of the possibilities, mechanism, and results of the pyrolysis of a particular biomass representative. Based on those results, it can be stated that spongin is a promising source of naturally prefabricated, three-dimensional biocarbons for various purposes, and its carbonization to obtain a functional material is described in detail in **Publications 5-6**.

It should be mentioned that the application of spongin in material science was already thoughtfully studied within the framework of previously conducted two Ph.D. theses where the attention was paid to develop the novel photocatalysts or composites for electrochemical applications [228-229]. However, the possibility of using the spongin to support the metal-containing phase for catalytic oxidation-reduction reactions has not been investigated before. Therefore, **Publication 4** is concerned with the functionalization of spongin-based scaffolds with cobalt and silver by immobilization of particular ions followed by reduction with sodium borohydride, then the characterization of resulted composite materials and their application as heterogeneous catalysts in the standard reduction reaction of 4-nitrophenol to 4-aminophenol in water. Three different materials, labeled Co_spongin, Ag_spongin, and Co-Ag_spongin, were prepared, and the conditions of functionalization are showed in Table 5.

Table 5. *Conditions of the functionalization process.*

Prepared catalyst	Metal precursor	Functionalization conditions
Co_spongin	100 mL of 5 g/L solution of $Co(NO_3)_2$	3 g of spongin. Sorption 60 min at temp. 25 °C. Reduction with 0.1 mol/L solution of $NaBH_4$ dosed with speed 1 mL/min to existing mixture; reduction time 60 min The procedure was repeated three times.
Ag_spongin	100 mL of 5 g/L solution of $AgNO_3$	
Co-Ag_spongin	50 mL of g/L solution of $Co(NO_3)_2$ and 50 mL of 5 g/L solution of $AgNO_3$	

After functionalization, the materials were tested as potential catalysts in the reaction of reduction 4-nitrophenol to 4-aminophenol in the presence of sodium borohydride as a source of hydrogen. This reaction was chosen as a *"gold standard reaction"* to check the potential catalytic activity of metals particles from block d of the periodic table of elements. Even though this reaction is thermodynamically possible ($E_0|\text{4-NP/4-AP} = -0.76$ V, $E_0|H_3BO_3/BH_4 = -1.33$ V), the kinetics barriers stop the reaction to proceed without using a catalyst. Thus, the potential catalyst must play the role of an electronic relay system where the electron is transferred from BH_4^- donor groups towards 4-nitrophenol acceptor groups. Moreover, this reaction is 100% selective towards forming 4-aminophenol and can be carried out and monitored *in-situ* using the UV-Vis spectrophotometer.

Nonetheless, prior to catalytic tests, the effect of functionalization was checked by evaluation of the physicochemical properties of resulted composites. The SEM images obtained after functionalization exhibited the formation of agglomerates of the metal-containing phase. For Co_spongin and Co-Ag_spongin, the size of agglomerates does not exceed 2 μm, although, for Ag_spongin, the metal-containing phase was characterized by the formation of spherical particles with a size smaller than 1 μm. EDS analysis results confirmed the successful coverage of spongin-based scaffolds fibers with cobalt- or silver-containing phases with similar content equaled approx. 83%. Based on the data and Pourbaix diagrams of cobalt and silver, Co_3O_4 and metallic cobalt were suggested to represent the cobalt phase. At the same time, the silver-containing phase consists mainly of silver particles.

Interestingly, when both cations were presented during the functionalization, the spongin seemed to have a higher affinity to bind silver than cobalt. Thus, the content of silver is much higher than cobalt in the Co-Ag_spongin sample. Further analysis showed that prepared composites possess higher thermal stability than spongin-based scaffolds. FTIR analysis results showed that a wide variety of functional groups characteristic for spongin-based scaffolds is also present for composite materials. Although, due to the strong overlapping of Co-O groups, the particular bands typical for those vibrations are not present in the spectra of Co_spongin and Co-Ag_spongin. It was also stated that the amine groups from cysteine were mainly responsible for immobilizing silver and cobalt ions on the surface of spongin-based scaffolds.

The focal point of **Publication 4** was to evaluate the prepared composites as a possible catalyst, and the activity of particular materials is depicted in Fig. 16.

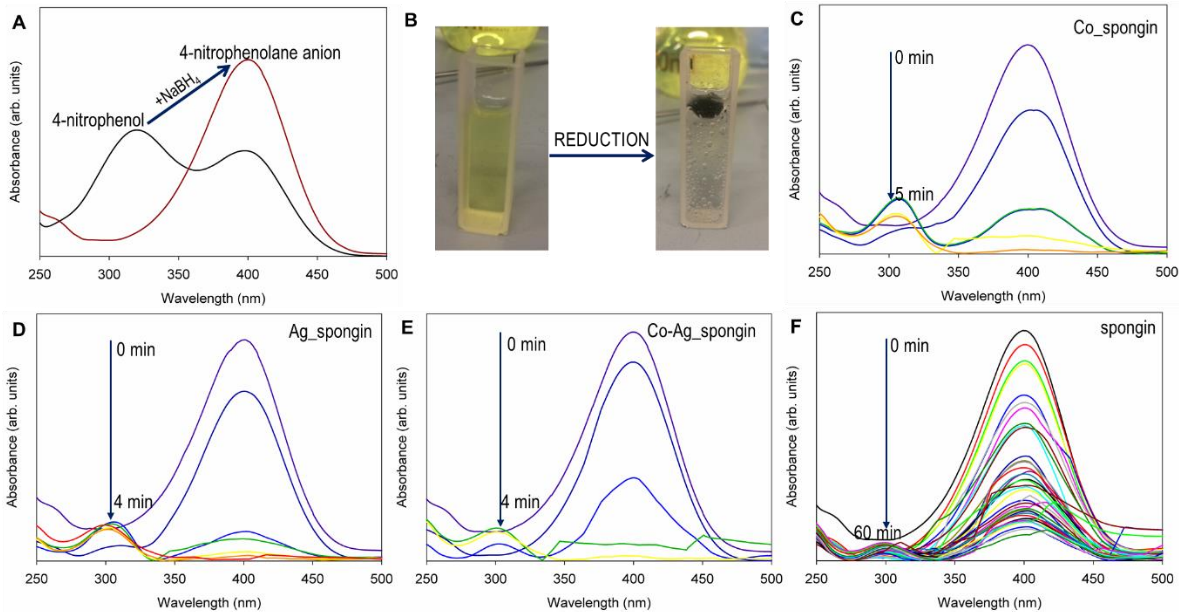


Fig. 16. *UV-Vis spectra of 4-nitrophenol and 4- nitrophenolate anion (A); the reaction mixture before reaction (left) and after the reduction (right) (B); UV-Vis spectra of reduction of 4-nitrophenol after addition of NaBH4 in the presence of different catalysts: Co_spongin (C), Ag_spongin (D), Co-Ag_spongin (E) and spongin (F).*

In the beginning, 0.5 mL of water solution of $NaBH_4$ was introduced to 2.5 mL of the solution of 4-nitrophenol, which results in the color change from pale yellow to dark yellow (see Fig. 16B) and shift of the absorbance maxima to 400 nm – which is characteristic for the 4-nitrophenolate anions. Consequently, the intensity of this band is further evaluated. The 5 mg of the prepared catalyst was introduced to the cuvette to start the reaction. Depending on the catalyst used, the 100% reduction was achieved after 4 min (for Ag_spongin and Ag-Co_spongin) or 5 min for Co-spongin. Interestingly, the non-functionalized spongin-based scaffolds were also used in the same reaction, where after 60 min of reaction, the reduction efficiency was equaled 65%. The shape of spectra proved that the 4-nitrophenol is gradually transformed into 4-aminophenol. Such extraordinary activity of spongin-based scaffolds may be connected to the presence of hydroxyl and amide functional groups, which can enhance the sorption of reagents and serve as an electron relay system. However, such a long reaction time excluded spongin from being considered as an effective catalyst.

On the other hand, the functionalization with silver and cobalt led to obtaining active catalysts. The metal-containing phase catalyzes the formation of hydrogen from borohydride anion or because of the formation of an effective electron relay system. Nevertheless, spongin might be considered an "active support" that can assist reagent sorption and electron transfer. In the next part of the work, the kinetics of the reduction was calculated using zero- and pseudo-first-order reaction models, where the linear equations are presented below:

$$\frac{C_t}{C_0} = -k \cdot t \tag{4}$$

$$\ln\left(\frac{C_t}{C_0}\right) = \ln(C_0) - k \cdot t \tag{5}$$

The experimental data are in agreement with the pseudo-first-order model. Thus, the calculated rate constants were evaluated based on this model. Interestingly the calculated rate constant for Ag_spongin was the lowest, even though the reduction with Co_spongin was one minute longer. Such results may be explained by the strongest interactions of silver particles with cysteine groups that could hamper the reduction efficiency. Moreover, for the Co-Ag_spongin composite, the calculated rate constant has the highest value, proving that the combination of two metal-containing phases forms an active catalyst where two phases can act synergistically. However, further reusability studies showed that the highest stability characterizes the Ag_spongin during repetitive use. For this material, the decrease in the value of the rate constant was insignificant. However, for Co- and Co-Ag_spongin, despite the high value of the rate constant in the first cycle, the value of constant rate decreases gradually after five repetitive reuses of those materials. The exceptional stability of silver over other prepared materials might be a consequence of the strong interaction between the silver particles and cysteine groups.

This work proved that spongin itself could be an effective support for the immobilization of metallic compounds active in reduction reactions, which was shown for the first time. However, due to the interesting three-dimensional fibrous morphology, the presence of various heteroatoms, and the relatively low activation energy of pyrolysis, spongin seems to be a great biomass precursor of naturally structured biocarbons that might have been suitable supports for metallic particles. Thus, **Publications 5-6** evaluated this possibility by performing the low-temperature pyrolysis and functionalization with cobalt and nickel moieties. Such an approach of low-temperature pyrolysis was never applied before for spongin-based scaffolds. Therefore, the novelty aspect of mentioned publications deals with the new route of using spongin-based scaffolds, their functionalization, and application in various oxidation-reduction reactions.

Spongin-based scaffolds were carbonized at relatively low temperatures 400 °C, 500 °C, and 600 °C and then modified using the same approach of immobilization followed by the reduction. The low carbonization temperatures were chosen to preserve the heteroatoms in the structure of resulted biocarbons because their presence would enhance the variety of surface functional groups after functionalization. Consequently, in **Publication 5,** the resulted biocarbons were modified with cobalt to obtain the materials mostly covered by cobalt oxide Co_3O_4 as denoted Co_3O_4@C400, Co_3O_4@C500, and Co_3O_4@C600 (see Fig. 17). The results of XRD and XPS analysis proved that the cobalt-containing phase was also composed of other cobalt oxides (CoO and CoO_2) and the surface layer of $Co(OH)_2$. The energy-dispersive X-ray spectroscopy (EDS) analysis proved that the content of the cobalt-containing phase varied with support used, and it is in the range of 15.64-36.93%.

Interestingly, the highest coverage was observed for Co_3O_4@C500 material, equaled 36.93%. Such a result might arise from the highest surface area of biocarbon and its chemical composition (for comparison, see supplementary note of **Publication 5**). Microscopic studies proved that the carbonized fibers were densely covered with the Co_3O_4-containing phase. Taking a closer look at the morphology of the fibers, it is apparent that the metal-containing phase forms different structures depends on the support used. The Co_3O_4@C400 is characterized by rod-like, round-shaped aggregates having a length equaled 1 μm, while for Co_3O_4@C500, agglomerates have uneven shapes, but rod-like structures might also be distinguished.

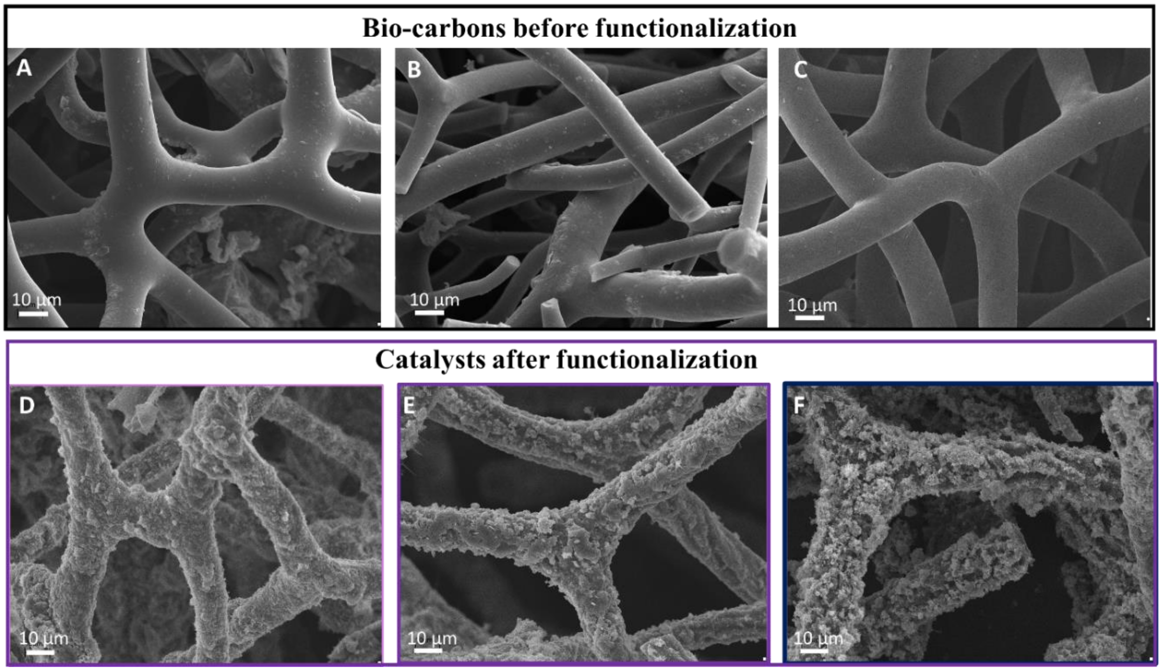


Fig. 17. *SEM investigation of bio-carbons obtained at temperatures: 400 °C (A), 500 °C (B), and 600 °C (C) with corresponding catalysts prepared during functionalization process* Co_3O_4*@C400 (D),* Co_3O_4*@C500 (E) and* Co_3O_4*@C600 (F).*

Interestingly, the surface of the fiber of Co_3O_4@C600 is covered with tiny rods and round shape particles aggregated in big structures. It seems that the increase of the cobalt content results in the aggregation of rod-like structures into larger systems and the formation of round-like crystallites. Interestingly, the measure BET surface area of prepared materials was not high and varied for different support. 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_3O_4@C600, respectively. The FTIR analysis revealed bands characteristic for vibrations of Co-O and O-Co-O bonds, among other groups derived from the biocarbons such as hydroxyl, amide, sulfoxide. The presence of sulfur and nitrogen was also confirmed using EDS and X-ray fluorescence spectroscopy (XRF) analyses. However, the FTIR spectra do not exhibit any features characteristic for silica and iron, which existence was shown using EDS and XRF techniques. Moreover, the results of XRF analysis revealed the presence of iodine and bromine even after carbonization at a temperature as high as 600 °C. Those results proved the diversity of the elemental composition and thus surface functional groups that might enhance the catalytic activity of prepared materials.

Consequently, in **Publication 5,** the focus was paid for utilization of prepared materials as potential catalysts in the oxidation of styrene, decolorization of rhodamine B, and, finally, reduction of 4-nitrophenol. The oxidation of styrene was carried out using two oxidants: hydrogen peroxide and tert-butyl hydroperoxide (TBHP). The results are presented in Table 6.

Table 6. *Comparison of styrene oxidation efficiency for prepared catalysts with calculated rate constant.*

Catalyst	Oxidant	Styrene conversion, %	Styrene oxide selectivity, %	Benzaldehyde selectivity, %
Co_3O_4@C400	H_2O_2	19.8	-	76.8
Co_3O_4@C500		15.2	-	81.2
Co_3O_4@C600		20.0	-	98.8
Co_3O_4@C400	TBHP	86.7	74.6	-
Co_3O_4@C500		91.8	69.7	-
Co_3O_4@C600		93.2	72.4	-

Reaction conditions: ratio of H_2O_2 to styrene 3:1, the concentration of styrene 100 mmol, temperature 65 °C; the ratio of TBHP to styrene 2:1, the concentration of styrene 10 mmol/L, temperature 70 °C. Catalyst concentration 0.8 g/L reaction time 8 h.

Interestingly, using hydrogen peroxide as an oxidant, the overall styrene conversion did not exceed 20% - independently of reaction conditions or catalyst used. The main product of the oxidation was benzaldehyde, with a selectivity that exceeded 80%. Such low styrene conversion was a consequence of the fact that the primary reaction on the surface of the catalyst was the decomposition of hydrogen peroxide, followed by the production of water molecules. Thus, the change of oxidant for TBHP resulted in increased styrene conversion from 86.75% for the Co_3O_4@C400 catalyst to 93.2% for Co_3O_4@C600. However, it should be mentioned that the change of oxidant resulted in the evolution of the reaction mechanism, where instead of benzaldehyde, which was not observed within the reaction products, the epoxide was the main product of oxidation. Selectivity varied with catalyst used and equaled 69.7% for Co_3O_4@C500, 74.6% for Co_3O_4@C400, and 72.4% for Co_3O_4@C600.

It should be noted that despite the highest content of the cobalt-containing phase, the Co_3O_4@C500 catalyst possesses surprisingly low catalytic ability toward styrene oxidation. It was stated that they could hamper the diffusion of substrates towards the catalyst's surface, considering the morphology of this material with huge agglomerates of cobalt oxide. In contrast, Co_3O_4@C600, with its more diversified morphology and larger average pore sizes that Co_3O_4@C500 seems to offer better accessibility of surface for reagents. Consequently, the reaction kinetics calculated using the second-order reaction model proved the exceptional activity of Co_3O_4@C600 in the oxidation of styrene, where the computed rate constant was equaled 0.0044 L/mmol·h. Finally, based on the literature, the oxidation mechanism was proposed (see Fig. 18).

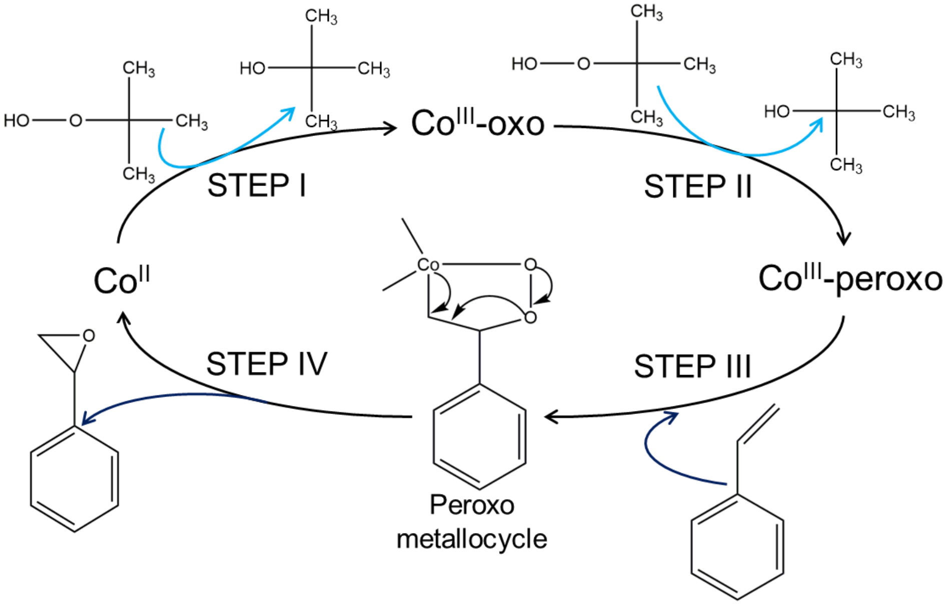


Fig. 18. *Proposed mechanism of styrene oxidation.*

In the first step, the TBHP molecules coordinate the Co sites forming Co^{III}-oxo species activated by the presence of TBHP molecules into Co^{III}-peroxo species. Consequently, the interactions between the styrene molecules and those species result in the formation of peroxo metallocycles to finally form styrene oxide molecules and the regeneration of Co^{III} sites.

To prove the versatility of prepared materials, they were used in catalytic decolorization of rhodamine B with hydrogen peroxide and reduction of 4-nitrophenol with sodium borohydride. The decolorization of rhodamine B was carried out in acidic pH to prevent the aggregation of the dye molecules. The progress of each reaction was monitored by UV-Vis spectroscopy (Fig. 19).

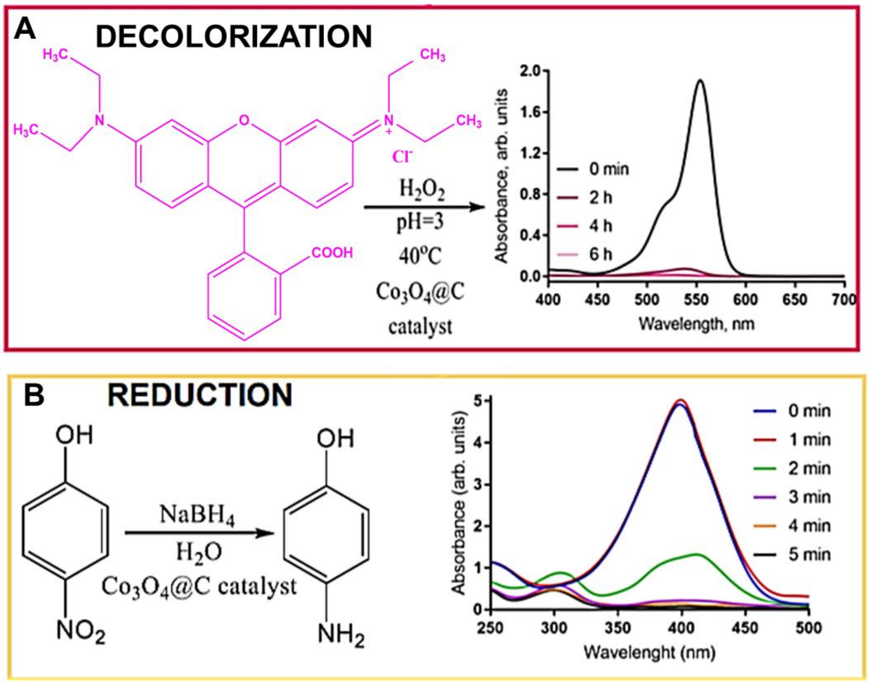


Fig. 19. *The representation of rhodamine B degradation and reduction of 4-nitrophenol with corresponding UV-Vis spectra [96].*

Decolorization results proved that after 2 hours of reaction, the value of λ_{max} typical for rhodamine B decreases gradually for every tested catalyst. Interestingly, it was found that the Co_3O_4@C500 catalyst exhibits the best decolorization ability, which can be a consequence of the highest content of the cobalt-containing phase. Thus, it seems that morphological issues do not seem to play an important role for this catalyst in this reaction. Moreover, the course of catalytic action was determined. The catalyst's surface plays a role of a place where the active radicals are formed, according to the pattern similar to the Fenton process, which can be described by the following reactions (1-3).

$$Co^{2+} + H_2O_2 + H^+ \leftrightarrow Co^{3+} + OH^{\cdot} + H_2O \quad (1)$$

$$OH^{\cdot} + H_2O_2 + \leftrightarrow HOO^{\cdot} + H_2O \quad (2)$$

$$Co^{3+} + HOO^{\cdot} \leftrightarrow Co^{2+} + O_2 + H^+ \quad (3)$$

The results of the 4-nitrophenol reduction proved that all prepared catalysts possess similar, high catalytic activity. Independently of the material used, the total reduction was achieved after 5 min of the reaction. The kinetics studies answer which catalyst might be considered as the most active. The pseudo-first-order reaction model was used (see equation 2 in **Publication 4**), due to the excessive amount of sodium borohydride applied in the reaction to calculate the reaction kinetics. Interestingly, calculated rate constants are similar for each catalyst; the values equaled 0.642 min^{-1} for Co_3O_4@C400, 0.742 min^{-1} for Co_3O_4@C500, and 0.755 min^{-1} for Co_3O_4@C600. Consequently, the Co_3O_4@C600 material was considered the most suitable for this reaction.

Moreover, during the catalytic study, the non-modified bio-carbons were tested to oxidize styrene and reduce 4-nitrophenol. However, it was shown that biocarbons possess activity either in styrene oxidation and 4-nitrophenol reduction, but the selectivity of oxidation and kinetics of reduction were significantly lower. Thus, it was stated that modification brings an advantage in a significant increase of the catalytic activity, but the supports might synergistically enhance those properties.

Notably, the reusability of the catalysts was tested for every reaction for catalyst showing the highest activity Co_3O_4@C600. Based on the results, a cobalt oxide-based catalyst can be successfully applied in an oxidation-reduction reaction several times without significant losing activity. However, the prolongation of reaction time was significant. On the other hand, for the reduction of 4-nitrophenol, it was proved that the calculated effectiveness of reaction after 5 minutes of reduction was high – equaled 90%. It could be explained by the partial deactivation of catalysts during repetitive reuse. Nevertheless, results obtained within the framework of **Publication 5** are significant considering that in the existing literature, oxidation-reduction reactions of environmentally emerging contaminants are carried out using complicated oxidation systems or photocatalytic processes.

The successful functionalization with cobalt inclines the extend of studies and test the possibility of biocarbons modification with nickel hydroxide, oxide, and metallic nickel. Consequently, three NiO/$Ni(OH)_2$/Ni-carbonized spongin-based materials were prepared via simple sorption–reduction method and named NiO/$Ni(OH)_2$/Ni_400, NiO/$Ni(OH)_2$/Ni_500 and NiO/$Ni(OH)_2$/Ni_600, respectively to the temperature of support carbonization. Consequently, prepared materials were utilized as potential catalysts in the oxidation-reduction reactions of various phenolic compounds: 4-nitrophenol, 4-chlorophenoxyacetic acid (4-CPA), methylchlorophenoxypropionic acid (MCPP), and phenol.

The phase composition was evaluated using XRD and XPS studies. The surface content of the nickel-containing phase was estimated to be in the range 15.2–26.0 wt% - according to the results of EDS measurement. Moreover, various heteroatoms, including nitrogen, sulphur, oxygen, iron, silica, and aluminium, were shown. Such varied chemical composition is responsible for the high diversity of surface functional groups, as was proved using FTIR analysis. The scanning electron microscopy investigation revealed interesting features in fibers morphology (Fig. 20).

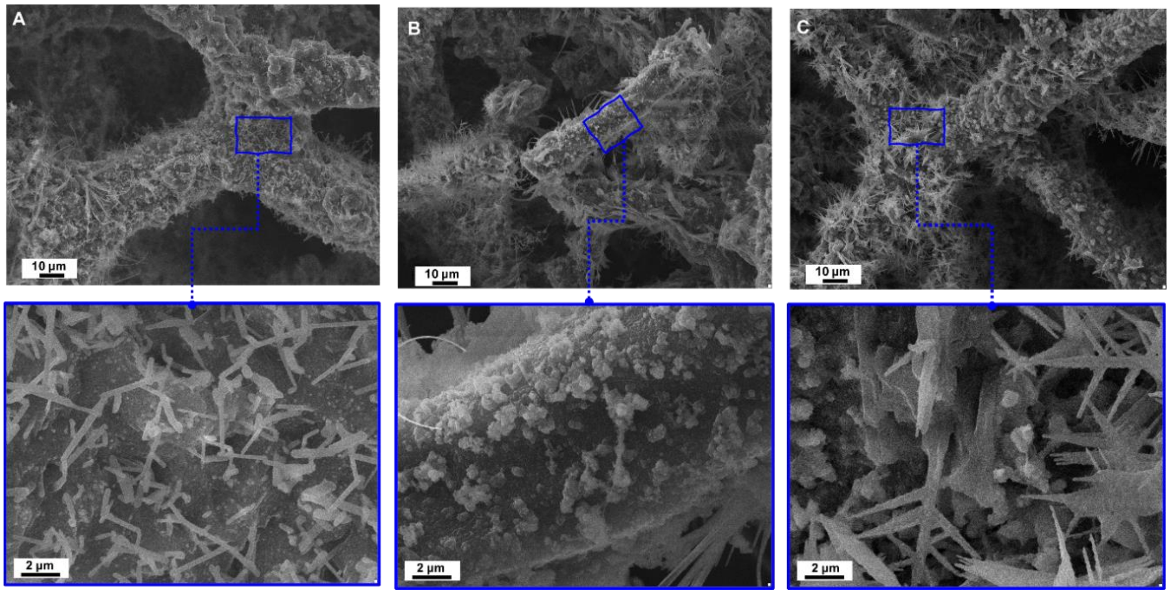


Fig. 20. *SEM investigation of prepared materials: NiO/Ni(OH)$_2$/Ni_400 (A), NiO/Ni(OH)$_2$/Ni_500 (B), and NiO/Ni(OH)$_2$/Ni_600 (C), adapted from [100].*

With the increase of the nickel species loading, the structure of the metal-containing phase was significantly altered. The fiber's surface of NiO/Ni(OH)$_2$/Ni_500 (characterized by the lowest content of nickel moieties) is covered by spherical agglomerates. For NiO/Ni(OH)$_2$/Ni_400, the metal-containing phase is forming needle-like structures with a length around 3-5 μm. The surface of NiO/Ni(OH)$_2$/Ni_600 thick and long needle-like structures characterize the material, which has the highest nickel species loading. However, the TEM images revealed that the structure of the metal-containing phase in nanoscale is similar and composed of thin sheets. The development of porous structure is essential for the application of particular material in catalysis. Although, the described in **Publication 6** material possesses the low value of BET surface area, which does not exceed 10 m^2/g (see for comparison Fig. 5 in **Publication 6**). On the other hand, the three-dimensional, fibrous hierarchical structure of biocarbon with a well-developed system of channels can provide good diffusion of substrates towards the catalytic surface, despite the low porosity.

Because the prepared materials were investigated as potential catalysts for reactions carried out in the aqueous phase, the electrokinetic behavior of prepared materials was evaluated using the measure of zeta potential versus pH. The measured isoelectric point (IEP) equals 4.30, 4.41, and 5.79 for NiO/Ni(OH)$_2$/Ni_400, NiO/Ni(OH)$_2$/Ni_500 and NiO/Ni(OH)$_2$/Ni_600, respectively, and the protonation and deprotonation mechanism of hydroxyl groups of Ni(OH)$_2$ and NiO was proposed as follows (4-5)

$$-Ni-OH+\ H^{+}\rightarrow -Ni-OH_{2}^{+} \tag{4}$$

$$-Ni-OH+\ OH^{-}\rightarrow -Ni-O^{-}+H_{2}O \tag{5}$$

The results indicated that the coverage with nickel species and the content of electron releasing groups directly influence the value of the isoelectric point.

Thereupon, prepared materials were firstly evaluated as catalysts in the reduction of 4-nitrophenol in water with the presence of sodium borohydride as a source of hydrogen. The course of the reaction was monitored using UV-Vis spectroscopy. It was proved that all materials possess similar activity towards reduction of 4-nitrophenol, and the reaction time varied between 4-6 min. However, the course of reaction for each catalyst was different. The induction period was observed for NiO/Ni(OH)$_2$/Ni_400, which was related to the transformation of the surface charges.

Interestingly, for NiO/Ni(OH)$_2$/Ni_500, stepwise reduction of the peak intensity typical for 4-nitrophenolane anion was exhibited, while NiO/Ni(OH)$_2$/Ni_600 its gradual decrease was observed. Thus, it was suggested that surface-mediated hydrogen transfer plays a major role during the reduction process for these materials. Kinetics evaluations showed that, despite the content of nickel species, the NiO/Ni(OH)$_2$/Ni_400 possess the highest value of the rate constant, and thus, the highest activity towards 4-nitrophenol reduction. The surface morphology of this solid explained such a result. The needle-like structures are thinner and shorten for NiO/Ni(OH)$_2$/Ni_400 than for NiO/Ni(OH)$_2$/Ni_600 material; ergo, the accessibility to the surface of catalyst might be better for the NiO/Ni(OH)$_2$/Ni_400 solid. Not without significance is the presence of various heteroatoms in the support structure, which may create additional active catalyst centers.

The reusability studies performed for NiO/Ni(OH)$_2$/Ni_400 showed the prolongation of reaction time and decrease of the constant rate value, possibly due to the blocking of active sites of catalysts. Even after the fifth cycle, the rate constant calculated for NiO/Ni(OH)$_2$/Ni_400 was still higher than the rate constant obtained for the NiO/Ni(OH)$_2$/Ni_500 catalyst in its first cycle. Moreover, based on the existing knowledge and obtained results, the reduction mechanism was proposed.

Subsequently, the catalytic oxidation reactions were carried out in an aqueous phase, at different pH using phenol, methylchlorophenoxypropionic acid (MCPP), and 4-chlorophenoxyacetic acid (4 CPA) as substrates (Fig. 21).

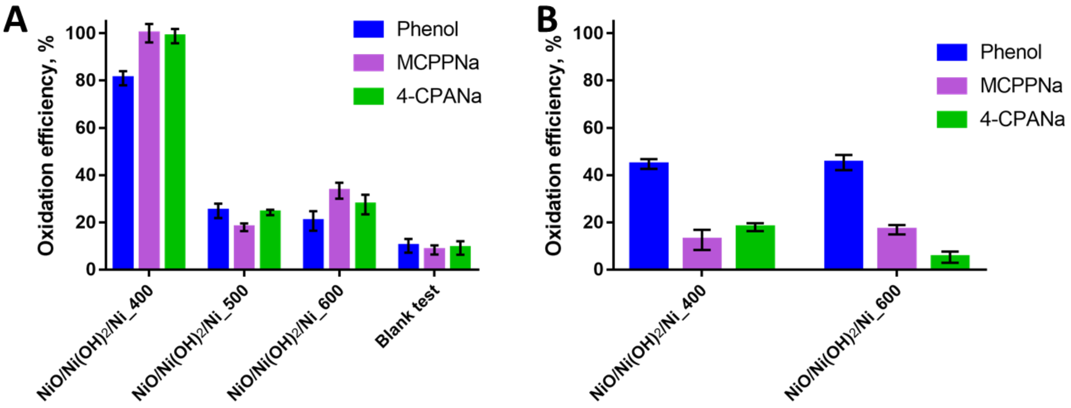


Fig. 21. *The efficiency of oxidation of phenol, MCPP, and 4-CPA using various carbonized spongin-based catalysts at pH 3 (A) and pH 8 (B) (concentration of substrate 0.0005 mol/L, catalyst concentration 1 g/L, time of reaction 4 h, 60 °C), adapted from [100].*

In contrast to the results of the reduction of 4-nitrophenol, where the differences in catalytic activity within the catalyst were relatively small, for oxidation reaction, the NiO/Ni(OH)$_2$/Ni_400 is showing the exceptional activity in the oxidation of MCPP and 4-CPA (oxidation yield more than 99%) and sufficient oxidation of phenol (oxidation yield 80%) at acidic pH. Interestingly, at the same reaction conditions, the effectiveness of oxidation for other catalysts does not exceed 40%. As was mentioned before, the exceptional activity of NiO/Ni(OH)$_2$/Ni_400 can be a consequence of favorable morphological structure, the biggest pore size among tested catalysts, and the chemical composition of biocarbon support. Interestingly, at basic pH, the yield of reactions is relatively low, which is an interesting finding considering the effect of pH on the protonation/deprotonation of the catalysts. It was proved that despite acidic pH, the oxidation process is not hampered by the repulsive electrostatic interaction between the substrate molecules and the catalyst surface significantly. Likewise, the prepared materials catalyzed the formation of hydroxyl radicals (at pH 3) or hydroxyl ions (at pH 8), which participate in the oxidation of phenolic compounds. Therefore, an increase in the pH of the reaction mixture has a significant negative effect on oxidation efficiency.

Due to the exceptional catalytic activity of NiO/Ni(OH)$_2$/Ni_400, the reusability tests were carried out only for this catalyst. After five catalytic runs, the decrease of oxidation efficiency of MCPP and 4-CPA reached 80% and 40% for phenol. As mentioned before, the significant reduction of efficiency could be related to loss of catalytic mass or poisoning of its active sites. The latter can be significant, especially for MCPP and 4-CPA, where the intermediate oxidation products contain chloride. Moreover, based on HPLC-MS results, the oxidation mechanism of MCPP and 4-CPA was proposed.

The most promising aspect of applying carbonized spongin-based scaffolds as a support for the metal-containing phase is their three-dimensional fibrous structure. The SEM images in **Publications 5 and 6** show this exceptional architecture of interlaced fibers, which create channels with different shapes: triangle-like, rectangular-like, pentagonal-like, and hexagonal-like – similar to those observed in honeycomb structures, with sizes I between 1 to 300 μm. In addition, the carbonization of those scaffolds does not lead to the breaking of their initial structure. Thus, they can be prepared in strictly designed shape. Moreover, spongin-based scaffolds are obtained from commercial sponges, which are cultivated worldwide, creating a sponge market worth more than US$20 million.

Spongin-based scaffolds are without a doubt great material for application in heterogeneous catalysis either before or after carbonization. However, their pyrolysis led to the formation of structured biocarbons possessing excellent stability, robustness, and good physicochemical properties. Moreover, the relatively simple modification approach applied in **Publications 4-6**, which does not require the use of extreme synthesis conditions or hazardous and expensive reagents, creates more possibilities for the synthesis and modification of bio-inspired materials, which is definitely in line with the philosophy of sustainable development.

7. SUMMARY

The presented doctoral thesis is focused on:

1) the seeking and investigation of new sponge species having the skeleton made from chitin within Demosponginae sponge class;
2) evaluation of the spongin-based scaffolds pyrolysis and investigation their usefulness to produce the advanced composites based either on spongin on biocarbons received after its carbonization.

For the first time, it was shown 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*. Their detailed evaluation proved that isolated chitin resembles the shape of a sponge skeleton and is built from α-chitin polymorph. The studies pointed out the possibilities of evaluating these sponges as new, promising sources of chitin and secondary metabolites for pharmacy, tissue engineering, and materials science.

The investigation of spongin-based scaffolds began with evaluating its usefulness as a source for producing the biocarbons by calculating the kinetics of its thermal degradation using thermogravimetric analysis (TG). The kinetic parameters of the pyrolysis in a nitrogen atmosphere were calculated using standard methods, including a model-fitting approach (Coats–Redfern method) and the model-free iso-conversional Friedman, Kissinger–Akahira–Sunose (KAS), and Ozawa–Flynn–Wall (OFW) methods. The TG analysis revealed that this biomaterial's thermal degradation does not depend on the heating regime, and during pyrolysis, two weight losses can be observed. The analysis of gases released during thermal degradation allowed identifying the discharged compounds and described the pathway of the process. Kinetics studies showed that the chemical reaction model best described the experimental data of thermal degradation. The activation energies calculated by the Coats–Redfern method were in the range 39.3–48.7 kJ/mol, which is slightly lower than for the commercial polyurethane foams. Such comprehensive study of pyrolysis of spongin-based scaffolds with the attempt to mathematically describe the process, which has never been explained before in the literature, proved this biomaterial's potential to be a source for biocarbon production.

Furthermore, the spongin-based scaffolds were applied as a support for cobalt/cobalt oxide, silver particles, as well as cobalt/cobalt oxide–silver particles. The utilization of a spongin-based scaffold for such purposes was performed for the first time. The fibers of resulted composites were evenly covered with metal-containing phase particles forming the agglomerates of different shapes and sizes. Those materials were successfully utilized as catalysts in the reduction of 4-nitrophenol to 4-aminophenol in water. The profound kinetic and reusability studies proved that the functionalization with metallic particles led to obtaining materials with great catalytic performance, good reusability properties, and significantly higher thermal stability.

Consequently, considering the unique structure of spongin-based scaffolds and their physicochemical properties, they were applied to produce biocarbons utilized further to support different cobalt oxide-based catalysts. The carbonization was carried out at temperatures of 400 °C, 500 °C, and 600 °C, followed by metallization via the sorption-reduction method. The low-temperature spongin carbonization used to prepare functional materials was described for the first time. Various techniques including XPS, XRD, XRF, SEM+EDS, FTIR, low-temperature N_2 sorption isotherms were applied to characterize composites' physicochemical and morphological properties. Carbonized materials without functionalization were also studied, and their properties compared with the prepared composites. It has been proved that all prepared composites exhibited superior catalytic properties in the oxidation of styrene, decolorization of rhodamine B, and reduction of 4-nitrophenol. The studies showed that the temperature of carbonization directly impacts the final material's structure and chemical composition. Nevertheless, support and metal-containing phase synergistic effect was suggested as a primary reason for such superior catalytic activity. Moreover, the recycle studies performed for the most active material proved that it could be reused several times without significant loss of catalytical activity in each tested reaction.

A similar approach was used to prepare $Ni(OH)_2$/NiO/Ni-carbonized spongin composites. The functionalization with nickel species was performed for biocarbon also obtained at temperatures 400 °C, 500 °C, and 600 °C. The study focused on the deep morphological and physicochemical characterization of resulted materials and their testing as a potential catalyst of oxidation and reduction of various emerging phenolic compounds.

Such deep study was depicted for the first time. The catalytic evaluation showed that all prepared materials exhibited good activity in the reduction of 4-nitrophenol. A reaction mechanism was proposed: the decomposition of borohydride anions takes place on crystallites of nickel moieties, which served as an electron relay system. In the oxidation studies of phenol, methylchlorophenoxypropionic acid (MCPP), and 4-chlorophenoxyacetic acid (4-CPA), only one catalyst, namely $Ni(OH)_2$/NiO/Ni_400, exhibited great activity in acidic conditions with using hydrogen peroxide as a green oxidation agent. Consequently, it was stated that the enhanced catalytic activity of prepared materials might be related to the multiphase composition of the nickel-containing phase. That increases the variety of active centers of catalysts; evenly distributed metal-containing phase. Finally, the unique morphology of the metal-containing phase synergistically acts with the three-dimensional structure of support, enhancing the diffusion of reagents to the catalyst's surface.

The listed achievements confirm the practical character of the realized studies and introduce significant novelty to the field associated with the production, characterization, and practical application of materials based on spongin and chitin.

The presented studies contribute to the knowledge about marine sponges and are located in the context of contemporary research about biomimetic materials.

8. FUTURE OUTLOOK

Growing ecosystems pollutions and an increase in energy demand are among the most significant challenges of humankind in the XXI century. Therefore, the scientific efforts are focused on developing new methods, materials, and technologies that will be environmentally friendly, low-cost, and sustainable development concerned. Consequently, the evaluation of new sources of biomaterials such as chitin fits perfectly in the current social-ecological targets. However, the development and description of a chitin source with a pre-fabricated structure are not only important from the evolutionary biology point of view. But it is also crucial for material science to look for new chitin sources which do not need additional structurization methods. Consequently, it is just the beginning of the route to obtain the functional materials. It is not without significance that marine sponges can be easily cultivated, providing a renewable source of three-dimensional chitin. Consequently, seeking new chitin sources offers a wide range of opportunities to integrate sponges as a renewable source for material science, environmental protection, pharmacy, and tissue engineering on an industrial scale. Despite the vast potential of chitin, its application in tissue engineering still shows broad development prospects. The various chitin modification approaches – through chemical or physical modification – might allow the preparation of scaffolds with desired shapes and ideal degradation rates, which could be suitable for bone graft alternatives. Moreover, the bioactive factors can be incorporated easily to obtain beneficial properties for osteogenesis. Likewise, the chemical nature of chitin, the possibility of easy protonation and further functionalization opens new possibilities for utilization of this promising biomaterial.

However, several issues remained unsolved. The most critical aspect lies in the long time necessary for chitin isolation using a classical approach. Likewise, the secondary metabolites removed during the standard procedure are not utilized further and are mostly treated like wastes. However, the attempt to reduce chitin isolation time was successfully developed, although only for Verongiida sponges. Consequently, there is a space for evaluating a less time-consuming approach of simultaneous chitin and secondary metabolites isolation to explore the full potential of sponges.

The great potential of spongin-based scaffolds has been shown in several works already published. Moreover, their application does not cause a threat to the environment because species of commercial sponges are cultivated worldwide as well, creating a sponge marked worth more than US$20. Consequently, their utilization is environmentally and economically beneficial. Nevertheless, several aspects of applying spongin-based scaffolds to produce advanced composites or form carbonized materials should be investigated in the future. The atomistic simulation might be performed to provide an additional overview of the optimization of carbonization parameters. The evaluation of the pyrolysis mechanism can provide additional insight and represent a milestone in the optimization process and help to establish the carbonization conditions more suitable for further application in material engineering. The effects of additives might also be investigated to evaluate their impact on the properties of biocarbons. Further studies could be performed about the functionalization mechanism and application of other metallization methods, such as a photo-deposition approach to develop a new branch of bioinspired materials. Likewise, the functionalization of biocarbons obtained at higher temperatures seems to be interesting to investigate in the future to check how the development of the crystalline structure of resulted carbon impacted the properties of the final composite material.

Regarding catalytic studies, the detailed characterization of spent catalysts might be an exciting topic for evaluation, investigating the effect of catalytic actions on the changes in composite physicochemical properties and morphology. Moreover, the promising activity in oxidation-reduction reaction opens the possibility of evaluating those materials in other organic reactions, such as creating C-C bonds or reactions in the gas phase. Especially composites functionalized with nickel hydroxides and oxides seem to have great potential to be applied as a part of electrode systems in producing energy storage devices or advanced electrocatalysts. Likewise, the heat and current conduction of those materials shall be studied to prove their potential in other branches of chemistry.

Owing to the sustainable development philosophy, the utilization of biopolymers to produce advanced materials without employ harsh production conditions or expensive reagents has an excellent perspective for the future. Therefore, the results obtained within the thesis framework constitute a milepost in developing bio-inspired materials based on spongin and indicate the potential for further growth of this interesting topic.

9. REFERENCES

[1] Y. Bar-Cohen, Biomimetics - Using nature to inspire human innovation, Bioinspir. Biomin. 1 (2006) 1–12. https://doi.org/10.1088/1748-3182/1/1/P01.

[2] R. Breslow, Biomimetic chemistry: Biology as an inspiration, J. Biol. Chem. 284 (2009) 1337–1342. https://doi.org/10.1074/jbc.X800011200.

[3] O.P. Chakrabarti, H.S. Maiti, R. Majumdar, Biomimetic synthesis of cellular SiC based ceramics from plant precursor, Bull. Mater. Sci. 27 (2004) 467–470. https://doi.org/10.1007/BF02708565.

[4] J. M. Benyus, Biomimicry: Innovation inspired by nature, Perennial, New York, 1997.

[5] N. Suresh Kumar, R. Padma Suvarna, K. Chandra Babu Naidu, P. Banerjee, A. Ratnamala, H. Manjunatha, A review on biological and biomimetic materials and their applications, Appl. Phys. A 126 (2020) 445. https://doi.org/10.1007/s00339-020-03633-z.

[6] O.S. Bello, K.A. Adegoke, R.O. Oyewole, Biomimetic materials in our world: A review, IOSR J. Appl. Chem. 5 (2013) 22–35. https://doi.org/10.9790/5736-0532235.

[7] P. Fratzl, Biomimetic materials research: What can we really learn from nature's structural materials? J. R. Soc. Interface 4 (2007) 637–642. https://doi.org/10.1098/rsif.2007.0218.

[8] M. Shimomura, Engineering biomimetics: Integration of biology and nanotechnology, In: M. Matsumoto, Y. Umeda, K. Masui, S. Fukushige (eds), Design for Innovative Value Towards a Sustainable Society, Springer, Dordrecht, 2012. https://doi.org/10.1007/978-94-007-3010-6_186

[9] D. Enders, A.A. Narine, Lessons from nature: Biomimetic organocatalytic carbon-carbon bond formations, J. Org. Chem. 73 (2008) 7857–7870. https://doi.org/10.1021/jo801374j.

[10] L. Marchetti, M. Levine, Biomimetic catalysis, ACS Catal. 1 (2011) 1090–1118. https://doi.org/10.1021/cs200171u.

[11] M. Wysokowski, M. Motylenko, H. Stöcker, V.V. Bazhenov, E. Langer, A. Dobrowolska, K. Czaczyk, R. Galli, A.L. Stelling, T. Behm, Ł. Klapiszewski, D. Ambrożewicz, M. Nowacka, S.L. Molodtsov, B. Abendroth, D.C. Meyer, K.J. Kurzydłowski, T. Jesionowski, H. Ehrlich, An extreme biomimetic approach: hydrothermal synthesis of β-chitin/ZnO nanostructured composites, J. Mater. Chem. B. 1 (2013) 6469–6476. https://doi.org/10.1039/c3tb21186j.

[12] M. Wysokowski, M. Motylenko, V.V. Bazhenov, D. Stawski, I. Petrenko, A. Ehrlich, T. Behm, Z. Kljajic, A.L. Stelling, T. Jesionowski, H. Ehrlich, Poriferan chitin as a template for hydrothermal zirconia deposition, Front. Mater. Sci. 7 (2013) 248–260. https://doi.org/10.1007/s11706-013-0212-x.

[13] H. Ehrlich, Biological Materials of Marine Origin. Invertebrates, Springer, Cham, 2010.

[14] H. Ehrlich, Biomimetic potential of chitin-based composite biomaterials of poriferan origin, In: A.J. Ruys (eds), Biomimetic Biomaterials Structure and Applications, Woodhead Publishing, Cambridge, 2013. https://doi.org/10.1533/9780857098887.1.46

[15] H. Ehrlich, H. Worch, Sponges as natural composites: from biomimetic potential to development of new biomaterials, In: E. Hajdu (eds), Porifera Research: Biodiversity, Innovation and Sustainability, Museu Nacional, Rio de Janiero, 2007

[16] M. Wysokowski, T.J. Szalaty, T. Jesionowski, M. Motylenko, D. Rafaja, I. Koltsov, H. Stöcker, V.V. Bazhenov, H. Ehrlich, A.L. Stelling, J. Beyer, J. Heitmann, S. Petovic, M. Đurović, Extreme biomimetic approach for synthesis of nanocrystalline chitin-(Ti,Zr)O_2 multiphase composites, Mater. Chem. Phys. 188 (2017) 115–124. https://doi.org/10.1016/j.matchemphys.2016.12.038.

[17] M. Wysokowski, T. Behm, R. Born, V.V. Bazhenov, H. Meißner, G. Richter, K. Szwarc-Rzepka, A. Makarova, D. Vyalikh, P. Schupp, T. Jesionowski, H. Ehrlich, Preparation of chitin-silica composites by *in vitro* silicification of two-dimensional *Ianthella basta* demosponge chitinous scaffolds under modified Stöber conditions, Mater. Sci. Eng. C 33 (2013) 3935–3941. https://doi.org/10.1016/j.msec.2013.05.030.

[18] M. Wysokowski, M. Motylenko, J. Beyer, A. Makarova, H. Stöcker, J. Walter, R. Galli, S. Kaiser, D. Vyalikh, V.V. Bazhenov, I. Petrenko, A.L. Stelling, S.L. Molodtsov, D. Stawski, K.J. Kurzydłowski, E. Langer, M. V. Tsurkan, T. Jesionowski, J. Heitmann, D.C. Meyer, H. Ehrlich, Extreme biomimetic approach for developing novel chitin-GeO_2 nanocomposites with photoluminescent properties, Nano Res. 8 (2015) 2288–2301. https://doi.org/10.1007/s12274-015-0739-5.

[19] N.P.S. Chauhan, M. Gholipourmalekabadi, M. Mozafari, Fabrication of newly developed pectin–GeO_2 nanocomposite using extreme biomimetics route and its antibacterial activities, J. Macromol. Sci. Part A Pure Appl. Chem. 54 (2017) 655–661. https://doi.org/10.1080/10601325.2017.1317211.

[20] K.A. Derwin, S.F. Badylak, S.P. Steinmann, J.P. Iannotti, Extracellular matrix scaffold devices for rotator cuff repair, J. Shoulder Elb. Surg. 19 (2010) 467–476. https://doi.org/10.1016/j.jse.2009.10.020.

[21] J. Reed, L. Klumb, M. Koobatian, C. Viney, Biomimicry as a route to new materials: What kinds of lessons are useful? Philos. Trans. R. Soc. A Math. Phys. Eng. Sci. 367 (2009) 1571–1585. https://doi.org/10.1098/rsta.2009.0010.

[22] C. Viney, Natural silks: Archetypal supramolecular assembly of polymer fibres, Supramol. Sci. 4 (1997) 75–81. https://doi.org/10.1016/S0968-5677(96)00059-4.

[23] H. Ehrlich, M. Maldonado, T. Hanke, H. Meissner, R. Born, D. Scharnweber, H. Worch, Spongins: Nanostructural investigations and development of biomimetic material model, VDI Berichte (2003) 287–290.

[24] H. Ehrlich, M. Wysokowski, S. Żółtowska-Aksamitowska, I. Petrenko, T. Jesionowski, Collagens of poriferan origin, Mar. Drugs. 16 (2018) 1–21. https://doi.org/10.3390/md16030079.

[25] A. Levin, T.A. Hakala, L. Schnaider, G.J.L. Bernardes, E. Gazit, T.P.J. Knowles, Biomimetic peptide self-assembly for functional materials, Nat. Rev. Chem. 4 (2020) 615–634. https://doi.org/10.1038/s41570-020-0215-y.

[26] J. Hwang, Y. Jeong, J.M. Park, K.H. Lee, J.W. Hong, J. Choi, Biomimetics: Forecasting the future of science, engineering, and medicine, Int. J. Nanomedicine 10 (2015) 5701–5713. https://doi.org/10.2147/IJN.S83642.

[27] D.E. Glaser, C. Viney, Biomimetic Materials, In: Biomaterials Science an Introduction to Materials in Medicine, B.D. Ratner, A.S. Hoffman, F.J. Schoen. J.E. Lemons (eds), Elsevier, Amsterdam, 2013. https://doi.org/10.1016/B978-0-08-087780-8.00033-4.

[28] P. Mohammadi, A. Sesilja Aranko, C. Paul Landowski, W. Wagermaier, M.B. Linder, Biomimetic composites with enhanced toughening using silk inspired triblock proteins and aligned nanocellulose reinforcements, Sci. Adv. 5 (2019) 1–12. https://doi.org/10.1126/sciadv.aaw2541.

[29] J. Liu, Y. Chen, T. Han, M. Cheng, W. Zhang, J. Long, X. Fu, A biomimetic SiO_2@chitosan composite as highly-efficient adsorbent for removing heavy metal ions in drinking water, Chemosphere 214 (2019) 738–742. https://doi.org/10.1016/j.chemosphere.2018.09.172.

[30] J. Charnley, Present status of replacement therapy. Principles and practice in hip replacement, Proc. R. Soc. London Biol. Sci. 192 (1976) 191–198. https://doi.org/10.1098/rspb.1976.0006.

[31] Q. Zhang, X. Yang, P. Li, G. Huang, S. Feng, C. Shen, B. Han, X. Zhang, F. Jin, F. Xu, T.J. Lu, Bioinspired engineering of honeycomb structure - using nature to inspire human innovation, Prog. Mater. Sci. 74 (2015) 332–400. https://doi.org/10.1016/j.pmatsci.2015.05.001.

[32] L. Zhang, S. Ma, Y. Chen, Y. Wang, J. Ou, H. Uyama, M. Ye, facile fabrication of biomimetic chitosan membrane with honeycomb-like structure for enrichment of glycosylated peptides, Anal. Chem. 91 (2019) 2985–2993. https://doi.org/10.1021/acs.analchem.8b05215.

[33] T.A. Herbert, Method of making stainless steel honeycomb panels, Patent no. US-2940557-A, 1960.

[34] D.J. Fahey, M.E. Dunlap, R.J. Seidl, Thermal conductivity of paper honeycomb cores and sound absorption of sandwich panels, Technical Report, Madison, Wisconsin: U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, 1953.

[35] P. Bardhan, Ceramic honeycomb filters and catalysts, Curr. Opin. Solid State Mater. Sci. 2 (1997) 577–583. https://doi.org/10.1016/S1359-0286(97)80048-4.

[36] J.R. Vinson, Optimum design of composite honeycomb sandwich panels subjected to uniaxial compression, AIAA J. 24 (1986) 1690–1696. https://doi.org/10.2514/3.9502.

[37] T.C. Hales, The honeycomb conjecture, Discret. Comput. Geom. 25 (2001) 1–22. https://doi.org/10.1007/s004540010071.

[38] K.P. Gadkaree, Carbon honeycomb structures for adsorption applications, Carbon 36 (1998) 981–989. https://doi.org/10.1016/S0008-6223(97)00230-3.

[39] J. Broeng, S.E. Barkou, A. Bjarklev, J.C. Knight, T.A. Birks, P.S.J. Russell, Highly increased photonic band gaps in silica/air structures, Opt. Commun. 156 (1998) 240–244. https://doi.org/10.1016/S0030-4018(98)00470-2.

[40] H. Masuda, H. Masuda, K. Fukuda, K. Fukuda, Ordered metal nanohole arrays made by a two-step replication of honeycomb structures of anodic alumina, Science 268 (1995) 1466–1468.

[41] Y. Du, N. Yan, M.T. Kortschot, Light-weight honeycomb core sandwich panels containing biofiber-reinforced thermoset polymer composite skins: Fabrication and evaluation, Compos. Part B Eng. 43 (2012) 2875–2882. https://doi.org/10.1016/j.compositesb.2012.04.052.

[42] T. Lecuit, P.F. Lenne, Cell surface mechanics and the control of cell shape, tissue patterns and morphogenesis, Nat. Rev. Mol. Cell Biol. 8 (2007) 633–644. https://doi.org/10.1038/nrm2222.

[43] A.D. Marmorstein, V.L. Bonilha, S. Chiflet, J.M. Neill, E. Rodriguez-Boulan, The polarity of the plasma membrane protein RET-PE2 in retinal pigment epithelium is developmentally regulated, J. Cell Sci. 109 (1996) 3025–3034.

[44] G. Pawin, K.L. Wong, K.Y. Kwon, L. Bartels, A homomolecular porous network at a Cu(111) surface, Science 313 (2006) 961–962. https://doi.org/10.1126/science.1129309.

[45] R.W.M. de Voogd, N.J. Alvarez, B. Boury-Esnault, N. Carballo, J.L. Cárdenas, P. Díaz, M.-C. Dohrmann, M. Downey, R. Hajdu, E. Hooper, J.N.A. Kelly, M. Klautau, M. Manconi, R.de Voogd, N.J. Alvarez, B. Boury-Esnault, N. Carballo, J.L. Cárdenas, World Porifera Database, (2021). https://doi.org/10.14284/359.

[46] D. Elieh-Ali-Komi, M.R. Hamblin, Chitin and chitosan: Production and application of versatile biomedical nanomaterials, Int. J. Adv. Res. 4 (2016) 411–427. https://doi.org/10.1016/j.cogdev.2010.08.003

[47] H.J. Blumenthal, S. Roseman, Quantitative estimation of chitin in fungi, J. Bacteriol. 74 (1957) 222–224

[48] M.V. Elorza, H. Rico, Sentandreu, Calcofluor White alters the assembly of chitin fibrils in *Saccharomyces cerevisiae* and *Candida albicans* cells, J. Gen. Microbiol. 129 (1983) 1577–1582.

[49] E. Brunner, P. Richthammer, H. Ehrlich, S. Paasch, P. Simon, S. Ueberlein, K.H. Van Pée, Chitin-based organic networks: An integral part of cell wall biosilica in the diatom *thalassiosira pseudonana*, Angew. Chemie Int. Ed. 48 (2009) 9724–9727. https://doi.org/10.1002/anie.200905028

[50] C.A. Durkin, T. Mock, E.V. Armbrust, Chitin in diatoms and its association with the cell wall, Eukaryot. Cell. 8 (2009) 1038–1050. https://doi.org/10.1128/EC.00079-09.

[51] P.C.J. Brunet, D.B. Carlisle, Chitin in pogonophora, Nature 182 (1958) 1689. https://doi.org/10.1038/1821689a0.

[52] S. Żółtowska, C. Klinger, I. Petrenko, M. Wysokowski, Y. Joseph, T. Jesionowski, H. Ehrlich, Methods of isolating chitin from sponges (porifera), In: Chitin and Chitosan: Properties and Applications, L.A.M. van den Broek, C.G. Boeriu (eds), John Wiley & Sons, Hoboken, 2019. https://doi.org/10.1002/9781119450467.ch2.

[53] G. Tóth, L. Zechmeister, Chitin content of the mandible of the snail (*Helix pomatia*), Nature 144 (1939) 1049. https://doi.org/10.1038/1441049c0.

[54] I.M. Weiss, V. Schönitzer, The distribution of chitin in larval shells of the bivalve mollusk *Mytilus galloprovincialis*, J. Struct. Biol. 153 (2006) 264–277. https://doi.org/10.1016/j.jsb.2005.11.006.

[55] S. Liu, J. Sun, L. Yu, C. Zhang, J. Bi, F. Zhu, M. Qu, C. Jiang, Q. Yang, Extraction and characterization of chitin from the beetle *Holotrichia parallela* motschulsky, Molecules 17 (2012) 4604–4611. https://doi.org/10.3390/molecules17044604.

[56] M. Mahdy Samar, M.H. El-Kalyoubi, M.M. Khalaf, M.M. Abd El-Razik, Physicochemical, functional, antioxidant and antibacterial properties of chitosan extracted from shrimp wastes by microwave technique, Ann. Agric. Sci. 58 (2013) 33–41. https://doi.org/10.1016/j.aoas.2013.01.006.

[57] H. Merzendorfer, Insect chitin synthases: A review, J. Comp. Physiol. B Biochem. Syst. Environ. Physiol. 176 (2006) 1–15. https://doi.org/10.1007/s00360-005-0005-3.

[58] H.O. Fabritius, C. Sachs, P.R. Triguero, D. Raabe, Influence of structural principles on the mechanics of a biological fiber-based composite material with hierarchical organization: The exoskeleton of the lobster *homarus americanus*, Adv. Mater. 21 (2009) 391–400. https://doi.org/10.1002/adma.200801219.

[59] M.M. Giraud-Guille, Fine structure of the chitin-protein system in the crab cuticle, Tissue Cell. 16 (1984) 75–92. https://doi.org/10.1016/0040-8166(84)90020-X.

[60] M.M. Giraud-Guille, H. Chanzy, R. Vuong, Chitin crystals in arthropod cuticles revealed by diffraction contrast transmission electron microscopy, J. Struct. Biol. 103 (1990) 232–240. https://doi.org/10.1016/1047-8477(90)90041-A.

[61] G.P. Wagner, J. Lo, R. Laine, M. Almeder, Chitin in the epidermal cuticle of a vertebrate (*Paralipophrys trigloides*, Blenniidae, Teleostei), Experientia 49 (1993) 317–319. https://doi.org/10.1007/BF01923410.

[62] J.W. Tang, J. Fernandez, J.J. Sohn, C.T. Amemiya, Chitin is endogenously produced in vertebrates, Curr. Biol. 25 (2015) 897–900. https://doi.org/10.1016/j.cogdev.2010.08.003.

[63] H. Ehrlich, M. Malando, K.-D. Spindler, C. Eckert, T. Hanke, R. Born, C. Goebel, P. Simon, S. Heinemann, H. Worch, first evidence of chitin as a component of the skeletal fibers of marine sponges. Part I. Verongidae (Demospongia: Porifera), J. Exp. Zool. B. Mol. Dev. Evol. 308 (2007) 347–356. https://doi.org/10.1002/jez.b.

[64] H. Ehrlich, M. Krautter, T. Hanke, P. Simon, C. Knieb, S. Heinemann, H. Worch, First evidence of the presence of chitin in skeletons of marine sponges. Part II. Glass sponges (Hexactinellida: Porifera), J. Exp. Zool. B Mol. Dev. Evol. 308B (2007) 473–483. https://doi.org/10.1002/jez.b.21174.

[65] H. Ehrlich, E. Steck, M. Ilan, M. Maldonado, G. Muricy, G. Bavestrello, Z. Kljajic, J.L. Carballo, S. Schiaparelli, A. Ereskovsky, P. Schupp, R. Born, H. Worch, V.V. Bazhenov, D. Kurek, V. Varlamov, D. Vyalikh, K. Kummer, V.V. Sivkov, S.L. Molodtsov, H. Meissner, G. Richter, S. Hunoldt, M. Kammer, S. Paasch, V. Krasokhin, G. Patzke, E. Brunner, W. Richter, Three-dimensional chitin-based scaffolds from Verongida sponges (Demospongiae: Porifera). Part II: Biomimetic potential and applications, Int. J. Biol. Macromol. 47 (2010) 141–145. https://doi.org/10.1016/j.ijbiomac.2010.05.009.

[66] H. Ehrlich, M. Ilan, M. Maldonado, G. Muricy, G. Bavestrello, Z. Kljajic, J.L. Carballo, S. Schiaparelli, A. Ereskovsky, P. Schupp, R. Born, H. Worch, V.V. Bazhenov, D. Kurek, V. Varlamov, D. Vyalikh, K. Kummer, V.V. Sivkov, S.L. Molodtsov, H. Meissner, G. Richter, E. Steck, S. Hunoldt, M. Kammer, S. Paasch, V. Krasokhin, G. Patzke, E. Brunner, Three-dimensional chitin-based scaffolds from Verongida sponges (Demospongiae: Porifera). Part I. Isolation and identification of chitin, Int. J. Biol. Macromol. 47 (2010) 141–145. https://doi.org/10.1016/j.ijbiomac.2010.05.009.

[67] E. Brunner, H. Ehrlich, P. Schupp, R. Hedrich, S. Hunoldt, M. Kammer, S. Machill, S. Paasch, V.V. Bazhenov, D.V. Kurek, T. Arnold, S. Brockmann, M. Ruhnow, R. Born, Chitin-based scaffolds are an integral part of the skeleton of the marine demosponge *Ianthella basta*, J. Struct. Biol. 168 (2009) 539–547. https://doi.org/10.1016/j.jsb.2009.06.018.

[68] J.A. Cruz-Barraza, J.L. Carballo, A. Rocha-Olivares, H. Ehrlich, M. Hog, Integrative taxonomy and molecular phylogeny of genus *Aplysina* (Demospongiae: Verongida) from Mexican Pacific, PLoS One 7 (2012). https://doi.org/10.1371/journal.pone.0042049.

[69] M. Wysokowski, V.V. Bazhenov, M.V. Tsurkan, R. Galli, A.L. Stelling, H. Stöcker, S. Kaiser, E. Niederschlag, G. Gärtner, T. Behm, M. Ilan, A.Y. Petrenko, T. Jesionowski, H. Ehrlich, Isolation and identification of chitin in three-dimensional skeleton of *Aplysina fistularis* marine sponge, Int. J. Biol. Macromol. 62 (2013) 94–100. https://doi.org/10.1016/j.ijbiomac.2013.08.039.

[70] H. Ehrlich, O.V. Kaluzhnaya, E. Brunner, M.V. Tsurkan, A. Ereskovsky, M. Ilan, K.R. Tabachnick, V.V. Bazhenov, S. Paasch, M. Kammer, R. Born, A. Stelling, R. Galli, S. Belikov, O.V. Petrova, V.V. Sivkov, D. Vyalikh, S. Hunoldt, G. Wörheide, Identification and first insights into the structure and biosynthesis of chitin from the freshwater sponge *Spongilla lacustris*, J. Struct. Biol. 183 (2013) 474–483. https://doi.org/10.1016/j.jsb.2013.06.015.

[71] H. Ehrlich, O.V. Kaluzhnaya, M.V. Tsurkan, A. Ereskovsky, K. Tabachnick, M. Ilan, A. Stelling, R. Galli, O.V. Petrova, S.V. Nekipelov, V.N. Sivkov, D. Vyalikh, R. Born, T. Behm, A. Ehrlich, L.I. Chernogor, S. Belikov, D. Janussen, V.V. Bazhenov, G. Wörheide, First report on chitinous holdfast in sponges (Porifera), Proc. R. Soc. B Biol. Sci. 280 (2013). https://doi.org/10.1098/rspb.2013.0339.

[72] T. Talevski, A. Talevska Leshoska, E. Pejoski, B. Pejin, T. Machałowski, M. Wysokowski, M. V. Tsurkan, O. Petrova, V. Sivkov, R. Martinovic, S. Pantovic, Y. Khrunyk, V. Trylis, A. Fursov, M. Djurovic, T. Jesionowski, H. Ehrlich, Identification and first insights into the structure of chitin from the endemic freshwater demosponge *Ochridaspongia rotunda* (Arndt, 1937), Int. J. Biol. Macromol. 162 (2020) 1187–1194. https://doi.org/10.1016/j.ijbiomac.2020.06.247.

[73] H. Ehrlich, V.V. Bazhenov, C. Debitus, N. de Voogd, R. Galli, M.V. Tsurkan, M. Wysokowski, H. Meissner, E. Bulut, M. Kaya, T. Jesionowski, Isolation and identification of chitin from heavy mineralized skeleton of *Suberea clavata* (Verongida: Demospongiae: Porifera) marine demosponge, Int. J. Biol. Macromol. 104 (2017) 1706–1712. https://doi.org/10.1016/j.ijbiomac.2017.01.141.

[74] S. Żółtowska-Aksamitowska, M.V. Tsurkan, S.C. Lim, H. Meissner, K. Tabachnick, L.A. Shaala, D.T.A. Youssef, V.N. Ivanenko, I. Petrenko, M. Wysokowski, N. Bechmann, Y. Joseph, T. Jesionowski, H. Ehrlich, The demosponge *Pseudoceratina purpurea* as a new source of fibrous chitin, Int. J. Biol. Macromol. 112 (2018) 1021–1028. https://doi.org/10.1016/j.ijbiomac.2018.02.071.

[75] H. Ehrlich, L.A. Shaala, D.T.A. Youssef, S. Żółtowska-Aksamitowska, M. Tsurkan, R. Galli, H. Meissner, M. Wysokowski, I. Petrenko, K. Tabachnick, V.N. Ivanenko, N. Bechmann, Y. Joseph, T. Jesionowski, Discovery of chitin in skeletons of non-verongiid Red Sea demosponges, PLoS One 13 (2018) 1–18. https://doi.org/10.1371/journal.pone.0195803.

[76] H. Ehrlich, L.A. Shaala, D.T.A. Youssef, S. Żółtowska-Aksamitowska, M. Tsurkan, R. Galli, H. Meissner, M. Wysokowski, I. Petrenko, K. Tabachnick, V.N. Ivanenko, N. Bechmann, Y. Joseph, T. Jesionowski, Discovery of chitin in skeletons of non-verongiid Red Sea demosponges, PLoS One 13 (2018) 1–18. https://doi.org/10.1371/journal.pone.0195803.

[77] J. Johnstone, Conditions of Life in the Sea: A Short Account of Quantitative Marine Biological Research, University Press, Cambridge, 1911

[78] C.P. Souza, B.C. Almeida, R.R. Colwell, I.N.G. Rivera, The importance of chitin in the marine environment, Mar. Biotechnol. 13 (2011) 823–830. https://doi.org/10.1007/s10126-011-9388-1.

[79] G. Gooday, The ecology of chitin degradation, In: Advances in Microbial Ecology Vol. 11, K.C. Marshall (eds), Plenum, New York, 1990.

[80] R. Jayakumar, M. Prabaharan, P.T. Sudheesh Kumar, S. V. Nair, H. Tamura, Biomaterials based on chitin and chitosan in wound dressing applications, Biotechnol. Adv. 29 (2011) 322–337. https://doi.org/10.1016/j.biotechadv.2011.01.005.

[81] P.R. Marreco, P. Da Luz Moreira, S.C. Genari, Â.M. Moraes, Effects of different sterilization methods on the morphology, mechanical properties, and cytotoxicity of chitosan membranes used as wound dressings, J. Biomed. Mater. Res. Part B Appl. Biomater. 71 (2004) 268–277. https://doi.org/10.1002/jbm.b.30081.

[82] N.L.B.M. Yusof, A. Wee, L.Y. Lim, E. Khor, Flexible chitin films as potential wound-dressing materials: Wound model studies, J. Biomed. Mater. Res. Part A 66 (2003) 224–232. https://doi.org/10.1002/jbm.a.10545.

[83] Y. Fan, T. Saito, A. Isogai, Preparation of chitin nanofibers from squid pen β-chitin by simple mechanical treatment under acid conditions, Biomacromolecules 9 (2008) 1919–1923. https://doi.org/10.1021/bm800178b.

[84] K. Gopalan Nair, A. Dufresne, Crab shell chitin whisker reinforced natural rubber nanocomposites. 1. Processing and swelling behavior, Biomacromolecules 4 (2003) 657–665. https://doi.org/10.1021/bm020127b.

[85] N.L.B. Muhammad Yusof, L.Y. Lim, E. Khor, Preparation and characterization of chitin beads as a wound dressing precursor, J. Biomed. Mater. Res. 54 (2001) 59–68. https://doi.org/10.1002/1097-4636(200101)54:1<59::AID-JBM7>3.0.CO;2-U.

[86] M. Prabaharan, Review paper: Chitosan derivatives as promising materials for controlled drug delivery, J. Biomater. Appl. 23 (2008) 5–36. https://doi.org/10.1177/0885328208091562.

[87] M. Prabaharan, R. Jayakumar, Chitosan-graft-β-cyclodextrin scaffolds with controlled drug release capability for tissue engineering applications, Int. J. Biol. Macromol. 44 (2009) 320–325. https://doi.org/10.1016/j.ijbiomac.2009.01.005.

[88] S. Kumari, R. Kishor, Chitin and chitosan: origin, properties, and applications, In: Handbook of Chitin and Chitosan, S. Gopi, S. Thomas, A. Pius (eds), Elseveir, Amsterdam, 2020. https://doi.org/10.1016/b978-0-12-817970-3.00001-8.

[89] M. Maldonado, Embryonic development of verongid demosponges supports the independent acquisition of spongin skeletons as an alternative to the siliceous skeleton of sponges, Biol. J. Linn. Soc. 97 (2009) 427–447. https://doi.org/10.1111/j.1095-8312.2009.01202.x.

[90] M. Gross, Magical mysteries of marine sponges, Curr. Biol. 31 (2021) R51–R54. https://doi.org/10.1016/j.cub.2020.12.031.

[91] T. Jesionowski, M. Norman, S. Żółtowska-Aksamitowska, I. Petrenko, Y. Joseph, H. Ehrlich, Marine spongin: Naturally prefabricated 3D scaffold-based biomaterial, Mar. Drugs. 16 (2018) 1–23. https://doi.org/10.3390/md16030088.

[92] E. Abderhalden, E. Strauss, Die Spaltprodukte des Spongins mit Säuren, Zeitschrift für Physiol. Chemie. 48 (1906) 49–53.

[93] V.J. Clancey, The constitution of sponges. The common bath sponge, *Hippospongia equina*, Biochem. J. 20 (1926) 1186–1189.

[94] R.J. Block, D. Bolling, The amino acid composition of keratins: The composition of gorgonin, spongin, turtle scutes, and another keratins, J. Biol. Chem. 127 (1939) 685–693.

[95] K.A. Piez, J. Gross, The amino acid composition and morphology of some invertebrate and vertebrate collagens, Biochim. Biophys. Acta 34 (1959) 24–39.

[96] S. Junqua, L. Robert, R. Garrone, M. Pavans de Ceccatty, J. Vacelet, Biochemical and morphological studies on collagens of horny sponges. *Ircinia filaments* compared to spongines, Connect. Tissue Res. 2 (1974) 193–203. https://doi.org/10.3109/03008207409152244.

[97] H. Ehrlich, R. Pallela, Marine Sponges: Chemicobiological and Biomedical Applications, Springer, New Delhi, 2016. https://doi.org/10.1007/978-81-322-2794-6.

[98] M. Norman, S. Żółtowska-Aksamitowska, A. Zgoła-Grześkowiak, H. Ehrlich, T. Jesionowski, Iron(III) phthalocyanine supported on a spongin scaffold as an advanced photocatalyst in a highly efficient removal process of halophenols and bisphenol A, J. Hazard. Mater. 347 (2018) 78–88. https://doi.org/10.1016/j.jhazmat.2017.12.055.

[99] S. Żółtowska, J.F. Miñambres, A. Piasecki, F. Mertens, T. Jesionowski, Three-dimensional commercial-sponge-derived Co_3O_4@C catalysts for effective treatments of organic contaminants, J. Environ. Chem. Eng. 9 (2021). https://doi.org/10.1016/j.jece.2021.105631.

[100] S. Żółtowska, Z. Bielan, J. Zembrzuska, K. Siwińska-Ciesielczyk, A. Piasecki, A. Zielińska-Jurek, T. Jesionowski, 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, Sci. Total Environ. 794 (2021) 148692. https://doi.org/10.1016/j.scitotenv.2021.148692.

[101] M. Norman, J. Zdarta, P. Bartczak, A. Piasecki, I. Petrenko, H. Ehrlich, T. Jesionowski, Marine sponge skeleton photosensitized by copper phthalocyanine: A catalyst for rhodamine B degradation, Open Chem. 14 (2016) 243–254. https://doi.org/10.1515/chem-2016-0025.

[102] B. Mayzel, J. Aizenberg, M. Ilan, The elemental composition of demospongiae from the Red Sea, Gulf of Aqaba, PLoS One 9 (2014). https://doi.org/10.1371/journal.pone.0095775.

[103] S. Żółtowska, M. Modelska, A. Piasecki, T. Jesionowski, Commercial sponges in heterogeneous catalysis: developing novel composites with cobalt and silver, Physicochem. Probl. Miner. Process. 56 (2020) 89–100. https://doi.org/10.37190/ppmp/126866.

[104] S. Żółtowska, I. Koltsov, K. Alejski, H. Ehrlich, M. Ciałkowski, T. Jesionowski, Thermal decomposition behaviour and numerical fitting for the pyrolysis kinetics

of 3D spongin-based scaffolds. The classic approach, Polym. Test. 97 (2021). https://doi.org/10.1016/j.polymertesting.2021.107148.

[105] M. Norman, P. Bartczak, J. Zdarta, H. Ehrlich, T. Jesionowski, Anthocyanin dye conjugated with *Hippospongia communis* marine demosponge skeleton and its antiradical activity, Dye. Pigment. 134 (2016) 541–552. https://doi.org/10.1016/j.dyepig.2016.08.019.

[106] M. Norman, P. Bartczak, J. Zdarta, W. Tomala, B. Żurańska, A. Dobrowolska, A. Piasecki, K. Czaczyk, H. Ehrlich, T. Jesionowski, Sodium copper chlorophyllin immobilization onto *Hippospongia communis* marine demosponge skeleton and its antibacterial activity, Int. J. Mol. Sci. 17 (2016). https://doi.org/10.3390/ijms17101564.

[107] J.C. Weaver, J. Aizenberg, G.E. Fantner, D. Kisailus, A. Woesz, P. Allen, K. Fields, M.J. Porter, F.W. Zok, P.K. Hansma, P. Fratzl, D.E. Morse, Hierarchical assembly of the siliceous skeletal lattice of the hexactinellid sponge *Euplectella aspergillum*, J. Struct. Biol. 158 (2007) 93–106. https://doi.org/10.1016/j.jsb.2006.10.027.

[108] Y. Khrunyk, S. Lach, I. Petrenko, H. Ehrlich, Progress in modern marine biomaterials research, Mar. Drugs 18 (2020) 12. https://doi.org/10.3390/md18120589.

[109] D. Louden, S. Inderbitzin, Z. Peng, R. de Nys, Development of a new protocol for testing bath sponge quality, Aquaculture 271 (2007) 275–285. https://doi.org/10.1016/j.aquaculture.2007.06.010.

[110] T. Szatkowski, M. Wysokowski, G. Lota, D. Pęziak, V.V. Bazhenov, G. Nowaczyk, J. Walter, S.L. Molodtsov, H. Stöcker, C. Himcinschi, I. Petrenko, A.L. Stelling, S. Jurga, T. Jesionowski, H. Ehrlich, Novel nanostructured hematite-spongin composite developed using an extreme biomimetic approach, RSC Adv. 5 (2015) 79031–79040. https://doi.org/10.1039/c5ra09379a.

[111] T. Szatkowski, K. Siwińska-Stefańska, M. Wysokowski, A.L. Stelling, Y. Joseph, H.Ehrlich, T. Jesionowski, Immobilization of titanium(IV) oxide onto 3D spongin scaffolds of marine sponge origin according to extreme biomimetics principles for removal of C.I. basic blue 9, Biomimetics 2 (2017) 4. https://doi.org/10.3390/biomimetics2020004.

[112] J. Zdarta, M. Norman, W. Smułek, D. Moszyński, E. Kaczorek, A.L. Stelling, H. Ehrlich, T. Jesionowski, Spongin-based scaffolds from *Hippospongia communis* demosponge as an effective support for lipase immobilization, Catalysts 7 (2017) 1–20. https://doi.org/10.3390/catal7050147.

[113] T. Szatkowski, K. Kopczyński, M. Motylenko, H. Borrmann, B. Mania, M. Graś, G. Lota, V.V. Bazhenov, D. Rafaja, F. Roth, J. Weise, E. Langer, M. Wysokowski, S. Żółtowska-Aksamitowska, I. Petrenko, S.L. Molodtsov, J. Hubálková,

C.G. Aneziris, Y. Joseph, A.L. Stelling, H. Ehrlich, T. Jesionowski, Extreme biomimetics: A carbonized 3D spongin scaffold as a novel support for nanostructured manganese oxide(IV) and its electrochemical applications, Nano Res. 11 (2018) 4199–4214. https://doi.org/10.1007/s12274-018-2008-x.

[114] I. Petrenko, A.P. Summers, P. Simon, S. Żółtowska-Aksamitowska, M. Motylenko, C. Schimpf, D. Rafaja, F. Roth, K. Kummer, E. Brendler, O.S. Pokrovsky, R. Galli, M. Wysokowski, H. Meissner, E. Niederschlag, Y. Joseph, S. Molodtsov, A. Ereskovsky, V. Sivkov, S. Nekipelov, O. Petrova, O. Volkova, M. Bertau, M. Kraft, A. Rogalev, M. Kopani, T. Jesionowski, H. Ehrlich, Extreme biomimetics: Preservation of molecular detail in centimeter-scale samples of biological meshes laid down by sponges, Sci. Adv. 5 (2019) 1–12. https://doi.org/10.1126/sciadv.aax2805.

[115] J. Bedia, M. Peñas-Garzón, A. Gómez-Avilés, J. Rodriguez, C. Belver, A review on the synthesis and characterization of biomass-derived carbons for adsorption of emerging contaminants from water, J. Carbon Research 4 (2018) 63. https://doi.org/10.3390/c4040063.

[116] S. De, A.M. Balu, J.C. Van Der Waal, R. Luque, Biomass-derived porous carbon materials: Synthesis and catalytic applications, ChemCatChem 7 (2015) 1608–1629. https://doi.org/10.1002/cctc.201500081.

[117] Z. Gao, Y. Zhang, N. Song, X. Li, Biomass-derived renewable carbon materials for electrochemical energy storage, Mater. Res. Lett. 5 (2017) 69–88. https://doi.org/10.1080/21663831.2016.1250834.

[118] J. Li, R. Xiao, M. Li, H. Zhang, S. Wu, C. Xia, Template-synthesized hierarchical porous carbons from bio-oil with high performance for supercapacitor electrodes, Fuel Process. Technol. 192 (2019) 239–249. https://doi.org/10.1016/j.fuproc.2019.04.037.

[119] Y. Liu, J. Chen, B. Cui, P. Yin, C. Zhang, Design and preparation of biomass-derived carbon materials for supercapacitors: A review, J. Carbon Res. 4 (2018) 53. https://doi.org/10.3390/c4040053.

[120] T.W. Eagar, Challenges in joining emerging materials, Proceedings of International Conference on Advances in Joining Newer Structural Materials, Montreal, Canada, 1990, Pergamon Press, Oxford, pp. 3–14.

[121] M. Kumar, X. Xiong, Y. Sun, I.K.M. Yu, D.C.W. Tsang, D. Hou, J. Gupta, T. Bhaskar, A. Pandey, Critical review on biochar-supported catalysts for pollutant degradation and sustainable biorefinery, Adv. Sustain. Syst. 1900149 (2020) 1–20. https://doi.org/10.1002/adsu.201900149.

[122] J.L. Figueiredo, Application of nanocarbon materials to catalysis, In: Nanotechnology in Catalysis: Applications in the Chemical Industry, Energy Development, and

Environment Protection, M. Van de Voorde, B. Sels (eds), Wiley-VCH Verlag, Weinheim, 2017. https://doi.org/10.1002/9783527699827.ch3.

[123] Y. Yang, K. Chiang, N. Burke, Porous carbon-supported catalysts for energy and environmental applications: A short review, Catal. Today 178 (2011) 197–205. https://doi.org/10.1016/j.cattod.2011.08.028.

[124] D.S. Su, S. Perathoner, G. Centi, Catalysis on nano-carbon materials: Going where to? Catal. Today 186 (2012) 1–6. https://doi.org/10.1016/j.cattod.2012.04.002.

[125] R. Shan, J. Han, J. Gu, H. Yuan, B. Luo, Y. Chen, A review of recent developments in catalytic applications of biochar-based materials, Resour. Conserv. Recycl. 162 (2020) 105036. https://doi.org/10.1016/j.resconrec.2020.105036.

[126] C. Askar, S. Baskar, R.S. Dhillon, Biomass Conversion: The Interface of Biotechnology, Chemistry and Materials Science, Springer Science+Business Media, New York, 2012.

[127] W.J. Liu, H. Jiang, H.Q. Yu, Development of biochar-based functional materials: Toward a sustainable platform carbon material, Chem. Rev. 115 (2015) 12251–12285. https://doi.org/10.1021/acs.chemrev.5b00195.

[128] M.A. Arsène, K. Bilba, H.S. Junior, K. Ghavami, Treatments of non-wood plant fibres used as reinforcement in composite materials, Mater. Res. 16 (2013) 903–923. https://doi.org/10.1590/S1516-14392013005000084.

[129] H.J. Huang, S. Ramaswamy, W. Al-Dajani, U. Tschirner, R.A. Cairncross, Effect of biomass species and plant size on cellulosic ethanol: A comparative process and economic analysis, Biomass Bioenergy 33 (2009) 234–246. https://doi.org/10.1016/j.biombioe.2008.05.007.

[130] F. Wang, D. Zhang, M. Chen, W. Yi, L. Wang, Characteristics of corn stover components pyrolysis at low temperature based on detergent fibers, Front. Bioeng. Biotechnol. 7 (2019) 1–9. https://doi.org/10.3389/fbioe.2019.00188.

[131] L. Leng, X. Yuan, G. Zeng, J. Shao, X. Chen, Z. Wu, H. Wang, X. Peng, Surface characterization of rice husk bio-char produced by liquefaction and application for cationic dye (malachite green) adsorption, Fuel 155 (2015) 77–85. https://doi.org/10.1016/j.fuel.2015.04.019.

[132] G. Omulo, N. Banadda, I. Kabenge, J. Seay, Optimizing slow pyrolysis of banana peels wastes using response surface methodology, Environ. Eng. Res. 24 (2019) 354–361. https://doi.org/10.4491/EER.2018.269.

[133] A.H. Faris, M.N.M. Ibrahim, A.A. Rahim, M.H. Hussin, N. Brosse, Preparation and characterization of lignin polyols from the residues of oil palm empty fruit bunch, BioResources 5 (2015) 3353–3355. https://doi.org/10.1109/igarss.2003.1294780.

[134] S.N.A.M. Hassan, M.A.M. Ishak, K. Ismail, S.N. Ali, M.F. Yusop, Comparison study of rubber seed shell and kernel (*Hevea brasiliensis*) as raw material for bio-oil production, Energy Procedia 52 (2014) 610–617. https://doi.org/10.1016/j.egypro.2014.07.116.

[135] W.L. Latshaw, E.C. Miller, Elemental composition of the corn plant, J. Agric. Res. 27 (1924) 845–861.

[136] L. Gao, H. Hu, X. Sui, C. Chen, Q. Chen, One for two: Conversion of waste chicken feathers to carbon microspheres and $(NH_4)HCO_3$, Environ. Sci. Technol. 48 (2014) 6500–6507. https://doi.org/10.1021/es5006708.

[137] W.M.F.W. Nawawi, M.P. Jones, E. Kontturi, A. Mautner, A. Bismarck, Plastic to elastic: Fungi-derived composite nanopapers with tunable tensile properties, Compos. Sci. Technol. 198 (2020) 108327. https://doi.org/10.1016/j.compscitech.2020.108327.

[138] M. Nayak, A. Karemore, R. Sen, Sustainable valorization of flue gas CO_2 and wastewater for the production of microalgal biomass as a biofuel feedstock in closed and open reactor systems, RSC Adv. 6 (2016) 9111–91120. https://doi.org/10.1039/c6ra17899e.

[139] B.H. León-Mancilla, M.A. Araiza-Téllez, J.O. Flores-Flores, M.C. Piña-Barba, Physico-chemical characterization of collagen scaffolds for tissue engineering, J. Appl. Res. Technol. 14 (2016) 77–85. https://doi.org/10.1016/j.jart.2016.01.001.

[140] X. Dang, M. Yang, B. Zhang, H. Chen, Y. Wang, Recovery and utilization of collagen protein powder extracted from chromium leather scrap waste, Environ. Sci. Pollut. Res. 26 (2019) 7277–7283. https://doi.org/10.1007/s11356-019-04226-x.

[141] R. Hao, H. Lan, C. Kuang, H. Wang, L. Guo, Superior potassium storage in chitin-derived natural nitrogen-doped carbon nanofibers, Carbon 128 (2018) 224–230. https://doi.org/10.1016/j.carbon.2017.11.064.

[142] J. McDonald-Wharry, M. Manley-Harris, K. Pickering, A comparison of the charring and carbonisation of oxygen-rich precursors with the thermal reduction of graphene oxide, Philos. Mag. 95 (2015) 4054–4077. https://doi.org/10.1080/14786435.2015.1108525.

[143] X.L. Zhou, H. Zhang, L.M. Shao, F. Lü, P.J. He, Preparation and application of hierarchical porous carbon materials from waste and biomass: A review, Waste Biomass Valori. 4 (2020) 1699–1724. https://doi.org/10.1007/s12649-020-01109-y.

[144] J. Deng, M. Li, Y. Wang, Biomass-derived carbon: Synthesis and applications in energy storage and conversion, Green Chem. 18 (2016) 4824–4854. https://doi.org/10.1039/c6gc01172a.

[145] M.S. Ahmad, Y. Nishina, Graphene-based carbocatalysts for carbon-carbon bond formation, Nanoscale 12 (2020) 12210–12227. https://doi.org/10.1039/d0nr02984j.

[146] R.M.M. Abbaslou, J. Soltan, A.K. Dalai, Effects of nanotubes pore size on the catalytic performances of iron catalysts supported on carbon nanotubes for Fischer-Tropsch synthesis, Appl. Catal. A Gen. 379 (2010) 129–134. https://doi.org/10.1016/j.apcata.2010.03.006.

[147] X. Wang, N. Li, J.A. Webb, L.D. Pfefferle, G.L. Haller, Effect of surface oxygen containing groups on the catalytic activity of multi-walled carbon nanotube supported Pt catalyst, Appl. Catal. B Environ. 101 (2010) 21–30. https://doi.org/10.1016/j.apcatb.2010.08.028.

[148] D.P. Upare, S. Yoon, C.W. Lee, Nano-structured porous carbon materials for catalysis and energy storage, Korean J. Chem. Eng. 28 (2011) 731–743. https://doi.org/10.1007/s11814-010-0460-8

[149] W. Yang, S. Chen, Biomass-derived carbon for electrode fabrication in microbial fuel cells: A review, Ind. Eng. Chem. Res. 59 (2020) 6391–6404. https://doi.org/10.1021/acs.iecr.0c00041.

[150] Y. Yang, X. Li, C. Zhou, W. Xiong, G. Zeng, D. Huang, C. Zhang, W. Wang, B. Song, X. Tang, X. Li, H. Guo, Recent advances in application of graphitic carbon nitride-based catalysts for degrading organic contaminants in water through advanced oxidation processes beyond photocatalysis: A critical review, Water Res. 184 (2020) 116200. https://doi.org/10.1016/j.watres.2020.116200.

[151] H. Jankowska, A. Swiatkowski, J. Choma, Active Carbon, Ellis Harwood, New York, 1991.

[152] P.N. Cheremisinoff, F. Ellerbusch, Carbon Adsorption Handbook, Ann Arbor Science, Ann Arbor, 1980..

[153] F. Rouquerol, J. Rouquerol, K. Sing, Adsorption by powders and porous solids. Second edition, Academic Press, San Diego, 1999.

[154] J. Hao, Y. Huang, C. He, W. Xu, L. Yuan, D. Shu, X. Song, T. Meng, Bio-templated fabrication of three-dimensional network activated carbons derived from mycelium pellets for supercapacitor applications, Sci. Rep. 8 (2018) 1–9. https://doi.org/10.1038/s41598-017-18895-6.

[155] B. Chang, W. Shi, H. Yin, S. Zhang, B. Yang, Poplar catkin-derived self-templated synthesis of N-doped hierarchical porous carbon microtubes for effective CO_2 capture, Chem. Eng. J. 358 (2019) 1507–1518. https://doi.org/10.1016/j.cej.2018.10.142.

[156] B. Fang, J.H. Kim, M. Kim, J.S. Yu, Ordered hierarchical nanostructured carbon as a highly efficient cathode catalyst support in proton exchange membrane fuel cell, Chem. Mater. 21 (2009) 789–796. https://doi.org/10.1021/cm801467y.

[157] J.H. Kim, B. Fang, M.S. Kim, S.B. Yoon, T.S. Bae, D.R. Ranade, J.S. Yu, Facile synthesis of bimodal porous silica and multimodal porous carbon as an anode catalyst support in proton exchange membrane fuel cell, Electrochim. Acta 55 (2010) 7628–7633. https://doi.org/10.1016/j.electacta.2009.10.079.

[158] Z. Bi, Q. Kong, Y. Cao, G. Sun, F. Su, X. Wei, X. Li, A. Ahmad, L. Xie, C.M. Chen, Biomass-derived porous carbon materials with different dimensions for supercapacitor electrodes: A review, J. Mater. Chem. A 7 (2019) 16028–16045. https://doi.org/10.1039/c9ta04436a.

[159] Y. Zhang, H. Chen, S. Wang, X. Zhao, F. Kong, Regulatory pore structure of biomass-based carbon for supercapacitor applications, Microporous Mesoporous Mater. 297 (2020) 110032. https://doi.org/10.1016/j.micromeso.2020.110032.

[160] Z. Li, D. Guo, Y. Liu, H. Wang, L. Wang, Recent advances and challenges in biomass-derived porous carbon nanomaterials for supercapacitors, Chem. Eng. J. 397 (2020) 125418. https://doi.org/10.1016/j.cej.2020.125418.

[161] Z. Li, L. Zhang, B.S. Amirkhiz, X. Tan, Z. Xu, H. Wang, B.C. Olsen, C.M.B. Holt, D. Mitlin, Carbonized chicken eggshell membranes with 3D architectures as high-performance electrode materials for supercapacitors, Adv. Energy Mater. 2 (2012) 431–437. https://doi.org/10.1002/aenm.201100548.

[162] M. Liang, R. Su, R. Huang, W. Qi, Y. Yu, L. Wang, Z. He, Facile in situ synthesis of silver nanoparticles on procyanidin-grafted eggshell membrane and their catalytic properties, ACS Appl. Mater. Interfaces 6 (2014) 4638–4649. https://doi.org/10.1021/am500665p.

[163] K. Nakajima, M. Hara, Amorphous carbon with SO_3H groups as a solid Brønsted acid catalyst, ACS Catal. 2 (2012) 1296–1304. https://doi.org/10.1021/cs300103k.

[164] S.K. Bhatia, R. Gurav, T.R. Choi, H.J. Kim, S.Y. Yang, H.S. Song, J.Y. Park, Y.L. Park, Y.H. Han, Y.K. Choi, S.H. Kim, J.J. Yoon, Y.H. Yang, Conversion of waste cooking oil into biodiesel using heterogenous catalyst derived from cork biochar, Bioresour. Technol. 302 (2020) 122872. https://doi.org/10.1016/j.biortech.2020.122872.

[165] H. Lyu, Q. Zhang, B. Shen, Application of biochar and its composites in catalysis, Chemosphere 240 (2020) 124842. https://doi.org/10.1016/j.chemosphere.2019.124842.

[166] H.K.D. Nguyen, V.V. Pham, H.T. Do, Preparation of Ni/biochar catalyst for hydrotreating of bio-oil from microalgae biomass, Catal. Letters. 146 (2016) 2381–2391. https://doi.org/10.1007/s10562-016-1873-8.

[167] J. Liu, J. Jiang, Y. Meng, A. Aihemaiti, Y. Xu, H. Xiang, Y. Gao, X. Chen, Preparation, environmental application and prospect of biochar-supported metal nanoparticles: A review, J. Hazard. Mater. 388 (2020) 122026. https://doi.org/10.1016/j.jhazmat.2020.122026.

[168] X. Li, C. Wang, J. Zhang, J. Liu, B. Liu, G. Chen, Preparation and application of magnetic biochar in water treatment: A critical review, Sci. Total Environ. 711 (2020) 134847. https://doi.org/10.1016/j.scitotenv.2019.134847.

[169] W. Ma, E.L. Kugler, D.B. Dadyburjor, Effect of properties of various activated-carbon supports and supported Fe-Mo-Cu-K catalysts on metal precursor distribution, metal reduction, and Fischer-Tropsch synthesis, Energy Fuels 24 (2010) 4099–4110. https://doi.org/10.1021/ef1003107.

[170] H. Zhang, W. Chu, C. Zou, Z. Huang, Z. Ye, L. Zhu, Promotion effects of platinum and ruthenium on carbon nanotube supported cobalt catalysts for Fischer-Tropsch synthesis, Catal. Lett. 141 (2011) 438–444. https://doi.org/10.1007/s10562-010-0536-4.

[171] C. Di Blasi, Modeling chemical and physical processes of wood and biomass pyrolysis, Prog. Energy Combust. Sci. 34 (2008) 47–90. https://doi.org/10.1016/j.pecs.2006.12.001.

[172] M.A. Islam, M. Asif, B.H. Hameed, Pyrolysis kinetics of raw and hydrothermally carbonized karanj (*Pongamia pinnata*) fruit hulls via thermogravimetric analysis, Bioresour. Technol. 179 (2015) 227–233. https://doi.org/10.1016/j.biortech.2014.11.115.

[173] R.K. Mishra, K. Mohanty, Pyrolysis kinetics and thermal behavior of waste sawdust biomass using thermogravimetric analysis, Bioresour. Technol. 251 (2018) 63–74. https://doi.org/10.1016/j.biortech.2017.12.029.

[174] L. Si, Y. Fan, Y. Wang, L. Sun, B. Li, C. Xue, H. Hou, Thermal degradation behavior of collagen from sea cucumber (*Stichopus japonicus*) using TG-FTIR analysis, Thermochim. Acta 659 (2018) 166–171. https://doi.org/10.1016/j.tca.2017.12.004.

[175] C.A. Miles, Kinetics of collagen denaturation in mammalian lens capsules studied by differential scanning calorimetry, Int. J. Biol. Macromol. 15 (1993) 265–271. https://doi.org/10.1016/0141-8130(93)90025-H.

[176] E. Senoz, R.P. Wool, C.W.J. McChalicher, C.K. Hong, Physical and chemical changes in feather keratin during pyrolysis, Polym. Degrad. Stab. 97 (2012) 297–307. https://doi.org/10.1016/j.polymdegradstab.2011.12.018.

[177] T.J. Szalaty, Ł. Klapiszewski, T. Jesionowski, Recent developments in modification of lignin using ionic liquids for the fabrication of advanced materials – A review, J. Mol. Liq. 301 (2020). https://doi.org/10.1016/j.molliq.2019.112417.

[178] Y. Yürüm, A. Taralp, T.N. Veziroglu, Storage of hydrogen in nanostructured carbon materials, Int. J. Hydrogen Energy 34 (2009) 3784–3798. https://doi.org/10.1016/j.ijhydene.2009.03.001.

[179] Robert W. Coughlin, Carbon as adsorbent and catalyst, Ind. Eng. Chem. Prod. Res. Dev. 8 (1969) 12–23.

[180] Y. Iwasawa, H. Nobe, S. Ogasawara, Reaction mechanism for styrene synthesis over polynaphthoquinone, J. Catal. 31 (1973) 444–449. https://doi.org/10.1016/0021-9517(73)90316-3.

[181] S. Navalon, A. Dhakshinamoorthy, M. Alvaro, H. Garcia, Carbocatalysis by graphene-based materials, Chem. Rev. 114 (2014) 6179–6212. https://doi.org/10.1021/cr4007347.

[182] D. Haag, H.H. Kung, Metal free graphene based catalysts: A review, Top. Catal. 57 (2014) 762–773. https://doi.org/10.1007/s11244-013-0233-9.

[183] H. Hu, J.H. Xin, H. Hu, X. Wang, Y. Kong, Metal-free graphene-based catalyst-insight into the catalytic activity: A short review, Appl. Catal. A General 492 (2015) 1-9. https://doi.org/10.1016/j.apcata.2014.11.041.

[184] Y. Wan, Y. Shi, D. Zhao, Supramolecular aggregates as templates: Ordered mesoporous polymers and carbons, Chem. Mater. 20 (2008) 932–945. https://doi.org/10.1021/cm7024125.

[185] P. Ehrburger, Dispersion of small particles on carbon surfaces, Adv. Colloid Interface Sci. 21 (1984) 275–302. https://doi.org/10.1016/0001-8686(84)85002-2.

[186] P.R. Gogate, A.B. Pandit, A review of imperative technologies for wastewater treatment I: Oxidation technologies at ambient conditions, Adv. Environ. Res. 8 (2004) 501–551. https://doi.org/10.1016/S1093-0191(03)00032-7.

[187] S. Navalon, M. Alvaro, H. Garcia, Heterogeneous Fenton catalysts based on clays, silicas and zeolites, Appl. Catal. B Environ. 99 (2010) 1–26. https://doi.org/10.1016/j.apcatb.2010.07.006

[188] A. Kubiak, K. Siwińska-Ciesielczyk, T. Jesionowski, Titania-based hybrid materials with ZnO, ZrO_2 and MoS_2: A review, Materials 11 (2018) 2295. https://doi.org/10.3390/ma11112295.

[189] D.S. Bhatkhande, V.G. Pangarkar, A.A.C.M. Beenackers, Photocatalytic degradation for environmental applications - A review, J. Chem. Technol. Biotechnol. 77 (2002) 102–116. https://doi.org/10.1002/jctb.532.

[190] U.I. Gaya, A.H. Abdullah, Heterogeneous photocatalytic degradation of organic contaminants over titanium dioxide: A review of fundamentals, progress and problems, J. Photochem. Photobiol. C Photochem. Rev. 9 (2008) 1–12. https://doi.org/10.1016/j.jphotochemrev.2007.12.003.

[191] S. Ahmed, M.G. Rasul, W.N. Martens, R. Brown, M.A. Hashib, Advances in heterogeneous photocatalytic degradation of phenols and dyes in wastewater: A review, Water. Air. Soil Pollut. 215 (2011) 3–29. https://doi.org/10.1007/s11270-010-0456-3.

[192] H.J.H. Fenton, Oxidation of tartatic acid in presence of iron, J. Chem. Soc. Trans. 65 (1894) 899–910.

[193] S. Wang, J. Wang, Peroxymonosulfate activation by Co_9S_8@S and N co-doped biochar for sulfamethoxazole degradation, Chem. Eng. J. 385 (2020) 123933. https://doi.org/10.1016/j.cej.2019.123933.

[194] W. Da Oh, S.K. Lua, Z. Dong, T.T. Lim, Performance of magnetic activated carbon composite as peroxymonosulfate activator and regenerable adsorbent via sulfate radical-mediated oxidation processes, J. Hazard. Mater. 284 (2015) 1–9. https://doi.org/10.1016/j.jhazmat.2014.10.042.

[195] J. Huang, H. Zhang, Mn-based catalysts for sulfate radical-based advanced oxidation processes: A review, Environ. Int. 133 (2019) 105141. https://doi.org/10.1016/j.envint.2019.105141.

[196] J. Li, Y. Li, Z. Xiong, G. Yao, B. Lai, The electrochemical advanced oxidation processes coupling of oxidants for organic pollutants degradation: A mini-review, Chinese Chem. Lett. 30 (2019) 2139–2146. https://doi.org/10.1016/j.cclet.2019.04.057.

[197] S. Guerra-Rodríguez, E. Rodríguez, D.N. Singh, J. Rodríguez-Chueca, Assessment of sulfate radical-based advanced oxidation processes for water and wastewater treatment: A review, Water 10 (2018) 1828. https://doi.org/10.3390/w10121828.

[198] J. Wang, S. Wang, Activation of persulfate (PS) and peroxymonosulfate (PMS) and application for the degradation of emerging contaminants, Chem. Eng. J. 334 (2018) 1502–1517. https://doi.org/10.1016/j.cej.2017.11.059.

[199] R.S. Ribeiro, A.M.T. Silva, J.L. Figueiredo, J.L. Faria, H.T. Gomes, Catalytic wet peroxide oxidation: A route towards the application of hybrid magnetic carbon nanocomposites for the degradation of organic pollutants. A review, Appl. Catal. B Environ. 187 (2016) 428–460. https://doi.org/10.1016/j.apcatb.2016.01.033.

[200] H.U. Blaser, A golden boost to an old reaction, Science 313 (2006) 312–313. https://doi.org/10.1126/science.1131574.

[201] M. Orlandi, D. Brenna, R. Harms, S. Jost, M. Benaglia, Recent developments in the reduction of aromatic and aliphatic nitro compounds to amines, Org. Process Res. Dev. 22 (2018) 430–445. https://doi.org/10.1021/acs.oprd.6b00205.

[202] B. Priewisch, K. Rück-Braun, Efficient preparation of nitrosoarenes for the synthesis of azobenzenes, J. Org. Chem. 70 (2005) 2350–2352. https://doi.org/10.1021/jo048544x.

[203] D. Formenti, F. Ferretti, F.K. Scharnagl, M. Beller, Reduction of nitro compounds using 3D-non-noble metal catalysts, Chem. Rev. 119 (2019) 2611–2680. https://doi.org/10.1021/acs.chemrev.8b00547

[204] R. V. Jagadeesh, K. Murugesan, A.S. Alshammari, H. Neumann, M.M. Pohl, J. Radnik, M. Beller, MOF-derived cobalt nanoparticles catalyze a general synthesis of amines, Science 358 (2017) 326–332. https://doi.org/10.1126/science.aan6245.

[205] A.I. Casoni, P.M. Hoch, M.A. Volpe, V.S. Gutierrez, Catalytic conversion of furfural from pyrolysis of sunflower seed hulls for producing bio-based furfuryl alcohol, J. Clean. Prod. 178 (2018) 237–246. https://doi.org/10.1016/j.jclepro.2018.01.031.

[206] Y.Y. Wang, L.L. Ling, H. Jiang, Selective hydrogenation of lignin to produce chemical commodities by using a biochar supported Ni-Mo_2C catalyst obtained from biomass, Green Chem. 18 (2016) 4032–4041. https://doi.org/10.1039/c6gc00247a.

[207] B. Sajjadi, A.A.A. Raman, H. Arandiyan, A comprehensive review on properties of edible and non-edible vegetable oil-based biodiesel: Composition, specifications and prediction models, Renew. Sustain. Energy Rev. 63 (2016) 62–92. https://doi.org/10.1016/j.rser.2016.05.035.

[208] S.H. Dhawane, T. Kumar, G. Halder, Recent advancement and prospective of heterogeneous carbonaceous catalysts in chemical and enzymatic transformation of biodiesel, Energy Convers. Manag. 167 (2018) 176–202. https://doi.org/10.1016/j.enconman.2018.04.073.

[209] A. Hidayat, Rochmadi, K. Wijaya, A. Nurdiawati, W. Kurniawan, H. Hinode, K. Yoshikawa, A. Budiman, Esterification of palm fatty acid distillate with high amount of free fatty acids using coconut shell char based catalyst, Energy Procedia 75 (2015) 969–974. https://doi.org/10.1016/j.egypro.2015.07.301.

[210] W. Xue, H. Zhao, J. Yao, F. Li, Y. Wang, Esterification of cyclohexene with formic acid over a peanut shell-derived carbon solid acid catalyst, Chinese J. Catal. 37 (2016) 769–777. https://doi.org/10.1016/S1872-2067(15)61076-2.

[211] S. Wang, R. Shan, Y. Wang, L. Lu, H. Yuan, Synthesis of calcium materials in biochar matrix as a highly stable catalyst for biodiesel production, Renew. Energy 130 (2019) 41–49. https://doi.org/10.1016/j.renene.2018.06.047.

[212] R.R.C. Bastos, A.P. da Luz Corrêa, P.T.S. da Luz, G.N. da Rocha Filho, J.R. Zamian, L.R.V. da Conceição, Optimization of biodiesel production using sulfonated carbon-based catalyst from an amazon agro-industrial waste, Energy Convers. Manag. 205 (2020) 112457. https://doi.org/10.1016/j.enconman.2019.112457.

[213] Y. Yuan, T. Yuan, D. Wang, J. Tang, S. Zhou, Sewage sludge biochar as an efficient catalyst for oxygen reduction reaction in a microbial fuel cell, Bioresour. Technol. 144 (2013) 115–120. https://doi.org/10.1016/j.biortech.2013.06.075.

[214] W. Yuan, Y. Feng, A. Xie, X. Zhang, F. Huang, S. Li, X. Zhang, Y. Shen, Nitrogen-doped nanoporous carbon derived from waste pomelo peel as a metal-free electrocatalyst for the oxygen reduction reaction, Nanoscale 8 (2016) 8704–8711. https://doi.org/10.1039/c6nr00764c.

[215] F. Zhang, J. Miao, W. Liu, D. Xu, X. Li, Heteroatom embedded graphene-like structure anchored on porous biochar as efficient metal-free catalyst for ORR, Int. J. Hydrogen Energy 44 (2019) 30986–30998. https://doi.org/10.1016/j.ijhydene.2019.09.239.

[216] K. Zhong, M. Li, Y. Yang, H. Zhang, B. Zhang, J. Tang, J. Yan, M. Su, Z. Yang, Nitrogen-doped biochar derived from watermelon rind as oxygen reduction catalyst in air cathode microbial fuel cells, Appl. Energy 242 (2019) 516–525. https://doi.org/10.1016/j.apenergy.2019.03.050.

[217] M. Li, H. Zhang, T. Xiao, S. Wang, B. Zhang, D. Chen, M. Su, J. Tang, Low-cost biochar derived from corncob as oxygen reduction catalyst in air cathode microbial fuel cells, Electrochim. Acta 283 (2018) 780–788. https://doi.org/10.1016/j.electacta.2018.07.010.

[218] A. Fukuoka, P.L. Dhepe, Catalytic conversion of cellulose into sugar alcohols, Angew. Chemie Int. Ed. 45 (2006) 5161–5163. https://doi.org/10.1002/anie.200601921.

[219] J.A. Bennett, N.J. Creamer, K. Deplanche, L.E. Macaskie, I.J. Shannon, J. Wood, Palladium supported on bacterial biomass as a novel heterogeneous catalyst: A comparison of Pd/Al_2O_3 and bio-Pd in the hydrogenation of 2-pentyne, Chem. Eng. Sci. 65 (2010) 282–290. https://doi.org/10.1016/j.ces.2009.06.069.

[220] W. Deng, X. Tan, W. Fang, Q. Zhang, Y. Wang, Conversion of cellulose into sorbitol over carbon nanotube-supported ruthenium catalyst, Catal. Lett. 133 (2009) 167–174. https://doi.org/10.1007/s10562-009-0136-3.

[221] H. Kobayashi, Y. Ito, T. Komanoya, Y. Hosaka, P.L. Dhepe, K. Kasai, K. Hara, A. Fukuoka, Synthesis of sugar alcohols by hydrolytic hydrogenation of cellulose over supported metal catalysts, Green Chem. 13 (2011) 326–333. https://doi.org/10.1039/c0gc00666a.

[222] M.G. Nijkamp, J.E.M.J. Raaymakers, A.J. Van Dillen, K.P. De Jong, Hydrogen storage using physisorption-materials demands, Appl. Phys. A Mater. Sci. Process. 72 (2001) 619–623. https://doi.org/10.1007/s003390100847.

[223] P.T Northcote, J.W. Blunt, M.H.G. Munro, Pateamine: A potent cytotoxin from the New Zealand Marine sponge, *Mycale* sp., Tetrahedron Lett. 32 (1991) 6411–6414.

[224] S. Matsunaga, T. Sugawara, N. Fusetani, New mycalolides from the marine sponge *Mycale magellanica* and their interconversion, J. Nat Prod. 61 (1998) 1164–1167.

[225] K. Ma, Y. Yang, Z. Deng, N.J. de Voogd, P. Proksch, W. Lin, Two new bromotyrosine derivatives from the marine sponge *Pseudoceratina* sp., Chem. Biodivers. 5 (2008) 1313–1320.

[226] M.S. Buchanan, A.R. Carroll, G.A. Fechner, A. Boyle, M. Simpson, R. Addepalli, V.M. Avery, J.N.A. Hooper, T. Cheung, H. Chen, R.J. Quinn, Aplysamine 6, an alkaloidal inhibitor of isoprenylcysteine carboxyl methyltransferase from the sponge *Pseudoceratina* sp., J. Nat. Prod. 71 (2008) 1066–1067.

[227] X.P. Huang, Z.W. Deng, R.W.M. Van Soest, W.H. Lin, Brominated derivatives from the Chinese sponge *Pseudoceratina* sp., J. Asian Nat. Prod. Res. 10 (2008) 239–242.

[228] T. Szatkowski, Hydrothermal synthesis of selected inorganic compounds using spongin-based scaffolds, PhD thesis, Poznan University of Technology, Faculty of Chemical Technology, Poland, 2017.

[229] M. Norman, Skeletons of selected marine demosponges as supports for dyes adsorption, PhD thesis, Poznan University of Technology, Faculty of Chemical Technology, Poland, 2018.

10. ATTACHMENTS

PUBLICATION 1

PUBLICATION 2

PUBLICATION 3

PUBLICATION 4

PUBLICATION 5

PUBLICATION 6

STATEMENTS
OF CO-AUTHORSHIP

POLITECHNIKA POZNAŃSKA

Sonia Żółtowska, M. Sc., Eng.
PhD Student
Faculty of Chemical Technology
Institute of Chemical Technology and Engineering
Berdychowo 4, PL-60 965 Poznan, Poland
e-mail address: sonia.zoltowska.aksamitowska@doctorate.put.poznan.pl

Poznań, 21.12.2021

Statement about the main contribution

Hereby, I confirm the contribution in the following publications:

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

My participation in publications 1 and 2 is estimated to be 35%. It includes carrying out the chitin isolation employing decalcification, demineralization, and desilicification processes, carrying out the Calcofluor white staining and fluorescence microscopy analysis, samples preparation for subsequent analysis, as well as preparation of the figures for the manuscript and following up with the review process.

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

My participation in publication 3 is estimated to be 55% and includes designing and performing the experiments, developing the kinetics calculations, preparing and writing the manuscript, and following up with the review process.

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

My participation in publication 4 is estimated to be 70%. It includes designing and performing the FTIR analysis and catalytic investigations, samples preparation for SEM+EDS and TG analyses, describing the results of the physicochemical studies and catalytic tests, preparing and writing the manuscript, and following up with the review process.

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

My participation in publication 5 is estimated to be 65%. It includes designing the experiments, performing the carbonization and functionalization of process spongin-based scaffolds, then carrying out the catalytic evaluation, performing FTIR, and potential zeta analyses, samples preparation for other analyses mentioned in the manuscript, describing the results of physicochemical studies and catalytic tests, preparing and writing the manuscript, and following up with the review process.

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

My participation in publication 6 is estimated to be 60%. It includes designing the experiments, performing the carbonization and functionalization of process spongin-based scaffolds, then carrying out the catalytic evaluation, performing FTIR, and potential zeta analysis, samples preparation for other analyses mentioned in the manuscript, describing the results of physicochemical studies and catalytic tests, preparing and writing the manuscript, and following up with the review process.

S. Żółtowska
....

....
Supervisor confirmation

POZNAN UNIVERSITY OF TECHNOLOGY

Professor Teofil Jesionowski, Ph.D., D.Sc., Eng.
Member of Polish Academy of Science
Rector
Head of Division of Chemical Technology
Faculty of Chemical Technology
Institute of Chemical Technology and Engineering
Berdychowo 4, PL-60965 Poznan, Poland
Tel.: +48616653720
e-mail: Teofil.Jesionowski@put.poznan.pl

25th October, 2021

Statement of co-authorship

I confirm the participation in the following publications:

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., 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
4) 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
5) 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
6) 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

My participation in publications 1 and 2 is estimated to be 5%, and in publications 3-6 is estimated to be 10% and includes coordination of research tasks and data interpretation with critical analysis.

Prof. Dr. rer. nat. habil. Hermann Ehrlich
Institute of Electronic and Sensor Materials
TU Bergakademie Freiberg
Gustav-Zeuner-Str. 3
09599 Freiberg, Germany

Freiberg, 22nd of November 2021

Statement of co-authorship

I confirm the participation in the following publications:

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., Elhady 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

My participation in publications 1-2 is estimated to be 5%, and in publication 3 is estimated to be 10%, including coordination of research tasks and results interpretation with critical analysis.

Hermann Ehrlich
Prof. Dr. habil

Dr hab. inż. Krzysztof Alejski, Professor of Poznan University of Technology
Institute of Chemical Technology and Engineering
Faculty of Chemical Technology
Poznan University of Technology
Berdychowo 4
60965 Poznan, Poland

Poznań, 27th of October 2021

Statement of co-authorship

I confirm the participation in the following publication:

1) 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

My participation is estimated to be 10% and includes critical analysis of data.

Dr. rer. nat. Nicole Bechmann
Faculty of Medicine Carl Gustav Carus
Dresden University of Technology
Fetscherstraße 74
01307 Dresden, Germany

Dresden, 8.11.2021

Statement of co-authorship

I confirm the participation in the following publications:

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

My participation in publications is estimated to be 5%, including critical analysis of data.

Nicole
Bechmann

Digitally signed by Nicole
Bechmann
DN: cn=Nicole Bechmann, c=DE,
o=UKDD,
email=nicole.bechmann@ukdd.de
Date: 2021.11.08 18:01:17 +01'00'

Dr inż. Zuzanna Bielan
Department of Process Engineering and Chemical Technology
Faculty of Chemistry
Gdansk University of Technology
Narutowicza 11/12,
PL-80233 Gdansk, Poland

Gdańsk, 25.10.2021

Statement of co-authorship

I confirm the participation in the following publication:

1) 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

My participation is estimated to be 5% and includes carrying out the XRD analysis.

Bielan
Zuzanna

Prof. dr hab inż. Michał Ciałkowski
Faculty of Environmental Engineering and Energy
Institute of Thermal Engineering
Poznan University of Technology
Piotrowo 3
60965 Poznan, Poland

Poznań 27th of October 2021

Statement of co-authorship

I confirm the participation in the following publication:

1) 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

My participation is estimated to be 10% and includes the studies of thermal degradation kinetics and critical data analysis.

Michał Ciałkowski

Ass. Prof. Dr. Sameh S. Elhady
Department of Natural Products
Faculty of Pharmacy
King Abdulaziz University
Jeddah 21589, Saudi Arabia

Jeddah, 8.11.2021

Statement of co-authorship

I confirm the participation in the following publication:

1) Żółtowska-Aksamitowska S., Shaala L.A., Youssef D.T.A., Elhady 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

My participation in the publication is estimated to be 5%, including critical analysis of data.

Sameh Said Elhady

9\11
2021

Viatcheslav N. Ivanenko, Ph.D.

Department of Invertebrate Zoology

Biological Faculty

Lomonosov Moscow State University

1-12 Leninskie Gory

119991 Moscow, Russia

Moscow, 8.11.2021

Statement of co-authorship

I confirm the participation in the following publications:

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

My participation in publications is estimated to be 5%, including critical analysis of data.

Slava Ivanenko

Prof. Dr. rer. nat. Yvonne Joseph
Institute of Electronic and Sensor Materials
TU Bergakademie Freiberg
Gustav-Zeuner-Str. 3
09599 Freiberg, Germany

Freiberg, 8.11.2021

Statement of co-authorship

I confirm the participation in the following publications:

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

My participation in publications is estimated to be 5%, including results interpretation with critical analysis.

TU Bergakademie Freiberg
Fakultät V
Institut für Elektronik- und Sensormaterialien
Gustav-Zeuner-Straße 3
D-09599 Freiberg/Sa.

Iwona Koltsov, PhD
Institute of High Pressure Physics
Polish Academy of Science
Sokołowska 29
01142 Warsaw, Poland

Warsaw, 8.11.2021

Statement of co-authorship

I confirm the participation in the following publication:

1) 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

My participation is estimated to be 5% and includes the performing TG-QMS analysis.

Iwona Koltsov

Dr. Heike Meißner
Faculty of Medicine Carl Gustav Carus
Dresden University of Technology
Fetscherstraße 74
01307 Dresden, Germany

Dresden, 8.11.2021

Statement of co-authorship

I confirm the participation in the following publications:

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

My participation in publications is estimated to be 5%, including carrying out the SEM analysis.

Heike Meißner

Prof. Dr. Florian Mertens
Institute of Physical Chemistry
TU Bergakademie Freiberg
Leipziger Straße 29
09599 Freiberg

Freiberg, 27th of October 2021

Statement of co-authorship

I confirm the participation in the following publication:

1) 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

My participation is estimated to be 5% and includes the critical analysis of data.

Prof. Dr. F. Mertens
TU Bergakademie Freiberg
Institut für Physikalische Chemie
Leipziger Straße 29
09599 Freiberg

Juan Francisco Miñambres Redondo, PhD
Department of Physical and Macromolecular Chemistry
Faculty of Science
Charles University
Hlavova 8,
12800 Prague, Czech Republic

Prague, 20.10.2021

Statement of co-authorship

I confirm the participation in following publication:

1) 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

My participation is estimated to be 15% and includes the performing of GC-FID analysis.

Juan Francisco Miñambres Redondo

Mgr inż. Martyna Modelska
Institute of Technology and Chemical Engineering
Faculty of Chemical Technology
Poznan University of Technology
Berdychowo 4
60965 Poznan, Poland

Poznan, 7.11.2021

Statement of co-authorship

I confirm the participation in the following publication:

1) 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

My participation is estimated to be 15% and includes synthesis of catalysts.

Martyna Modelska

Dr inż. Adam Piasecki
Institute of Materials Engineering
Poznan University of Technology
Piotrowo 3
61-138 Poznan, Poland

Poznan, 27th of October 2021

Statement of co-authorship

I confirm the participation in the following publications:

1) 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
2) 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
3) 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

My participation in publications is estimated to be 5% and includes carrying out the SEM-EDS analysis.

Dr. Yaroslav Petrenko

Institute of Electronic and Sensor Materials

TU Bergakademie Freiberg

Gustav-Zeuner-Str. 3

09599 Freiberg, Germany

Freiberg, 18.11.2021

Statement of co-authorship

I confirm the participation in the following publications:

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., Elhady 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

My participation in publications is estimated to be 5%, including results interpretation with critical analysis.

Dr. Iaroslav Petrenko

24.11.2021
Chemnitz, DE

Prof. Lamiaa Shaala
King Fahd Medical Research Center
King Abdulaziz University
Jeddah 21589
Saudi Arabia

Jeddah, 8.11.2021

Statement of co-authorship

I confirm the participation in the following publications:

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

My participation in publications is estimated to be 5%, including results interpretation with critical analysis.

Lamiaa

Dr hab. inż. Katarzyna Siwińska-Ciesielczyk
Institute of Technology and Chemical Engineering
Faculty of Chemical Technology
Poznan University of Technology
Berdychowo 4
60965 Poznan, Poland

Poznan, 8.11.2021

Statement of co-authorship

I confirm the participation in the following publication:

1) 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

My participation is estimated to be 5% and includes carrying out the BET analysis.

K. Siwińska-Ciesielczyk

Mr Lim Swee Cheng
St John's Island National Marine Laboratory
Tropical Marine Science Institute
National University of Singapore
18 Kent Ridge Road
Singapore 119227, Singapore

Singapore, 8.11.2021

Statement of co-authorship

I confirm the participation in the following publications:

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

My participation in publications is estimated to be 5%, including results interpretation with critical analysis.

Lim Swee Cheng
16/11/2021

Dr. Mikhail Tsurkan
Leibniz Institute of Polymer Research
Hohestraße 6
01069 Dresden, Germany

Dresden, 8.11.2021

Statement of co-authorship

I confirm the participation in the following publications:

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

My participation in publications is estimated to be 5%, including performing ESI-MS analysis with results interpretation.

/Mikhail Tsurkan, PhD

Dr inż. Marcin Wysokowski
Institute of Technology and Chemical Engineering
Faculty of Chemical Technology
Poznan University of Technology
Berdychowo 4
60965 Poznan, Poland

Poznan, 8.11.2021

Statement of co-authorship

I confirm the participation in the following publications:

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

My participation in publications is estimated to be 5%, including results interpretation with critical analysis.

Prof. Diaa T. A. Youssef
Department of Natural Products
Faculty of Pharmacy
King Abdulaziz University
Jeddah 21589, Saudi Arabia

Jeddah, 8.11.2021

Statement of co-authorship

I confirm the participation in the following publications:

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

My participation in publications is estimated to be 5%, including results interpretation with critical analysis.

Dr hab. inż. Joanna Zembrzuska
Institute of Chemistry and Technical Electrochemistry
Faculty of Chemical Technology
Poznan University of Technology
Berdychowo 4,
60965 Poznan, Poland

Poznań, 27th of October 2021

Statement of co-authorship

I confirm the participation in the following publication:

1) 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

My participation is estimated to be 15% and includes carrying out the HPLC-MS analysis and identification of degradation products.

Joanna Zembrzuska

Dr hab. inż. Anna Zielińska-Jurek, Professor Gdansk University of Technology
Department of Process Engineering and Chemical Technology
Faculty of Chemistry
Gdansk University of Technology
Narutowicza 11/12
PL-80233 Gdansk, Poland

Gdańsk, 27th of October 2021

Statement of co-authorship

I confirm the participation in the following publication:

1) 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

My participation is estimated to be 5% and includes analysis of data.

A. Zielińska-Jurek