Volume 9, Issue 2, 2020, 1004 - 1014 **ISSN 2284-6808**

Letters in Applied NanoBioScience

https://nanobioletters.com/

https://doi.org/10.33263/LIANBS92.10041014

Original Review Article **Open Access Journal**

Received: 16.04.2020 / Revised: 07.05.2020 / Accepted: 08.05.2020 / Published on-line: 10.05.2020

Poriferan chitin: 3D scaffolds from nano- to macroscale. A review

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ABSTRACT

Modern scaffolding strategy with respect to chitin is based on the application of naturally prefabricated 3D chitinous scaffolds of both aquatical and terrestrial invertebrates origin, mostly in the form of decellularized matrices. The sources of such constructs should be renewable or represent biodegradable and non-toxic waste materials. Sponges (Porifera) have been recognized among the first multicellular organisms on Earth having survived for more than 500 million yearsdue to their ability to synthetize robust skeletons with uniquely developed microporous 3D architecture and protect themselves from predatory microorganisms through the production of diverse secondary metabolites with multi-target biological activities. In this study, we analysed the occurrence of naturally pre-designed 3D chitinous matrices reported in sponges on nano-, micro- and macro-scale levels for the first time. Special focus is dedicated to the practical applications of such unique constructs in biomedicine.

Keywords:*chitin; scaffolds; marine sponges; tissue engineering; extreme biomimetics; biosorbents.*

1. INTRODUCTION

Chitin remains to be one of the abundant structural aminopolysaccharides in uni-and multi-cellular eukaryotes. It represents a straight chain polymer of N-acetylglucosamine (N-acetyl-2-amino-2-deoxy-D-glucose) units, joined to one another by 1,4-ßglucosidic bonds with chemical formula, $(C_6H_9O_4.NH.CO.CH_3)_n$. Chitin possesses a characteristic crystalline pattern and was confirmed to exist in alpha, beta and gamma allomorphs [1].

Its ancient origin has been recently demonstrated in the fossilised remnants of eukaryotic nature found in an 810–715 million year (myr) old dolomitic shale [2] as well as in 505 myr old *Vauxia gracilenta* demosponge fossil [3]. After initial reports on the presence of chitin in fungi and beetles had appeared in 1811 and 1826, respectively (see for overview [4]), this nanostructured biopolymer has been identified in diverse taxons, including protists, coralline algae, diatoms, sponges, bryozoans, corals, pogonophorans, annelids, molluscs, spiders, insects and crustaceans [5–11]. Although a few reports pointed to the existence of chitin in membrane-like structures of fish and amphibians [12,13], thorough analyses with strong evidence are needed to confirm this statement.

One of the obstacles to identifying chitin within biological structures is its occurrence mostly in the form of hybrid compounds (chitin-protein, chitin-polysaccharide, chitin-lipid, chitin pigment) [8,14] or mineral-containing biocomposites (chitin-silica, chitin-calcium carbonates) [6,10,15–26]. Consequently, today all known methodological approaches of chitin isolationare based on chemical, electrochemical (demineralization, deproteinization, depigmentation) and enzymatic treatments (see for overview [27,28]). Most of these approaches are still laborious, time-consuming and expensive. In contrast to other bio-macromolecules (i.e. proteins, pigments), the main crucial property of pure chitin lies in its strong resistance to harsh alkaline treatment up to the temperatures above 70°C, when chitin is transformed into chitosan due to its de-acetylation[29]. This property also played the principal role in the discovery of chitin in sponges (Porifera) in 2007 [15,30].

Figure 1. Chitin-based cell-free skeleton of *Aplysina aerophoba* demosponge (right fragment) becomes visible after selected treatment of the sponge body (left fragment) with 10% NaOH solution at 37°C during 24 h. Such skeletons have been used for isolation of pure chitin scaffolds with morphology that completely resembles their shape and size.

Despite the existence of numerous chitin-related books (see for a recent overview [11,31,32]) and important review papers concerning its identification, distribution, ecology, evolution, biosynthesis, genomics, characterization and applications [33–38],there is still no review on scaffolding strategies with respect to chitin from sponges. It should be noted, that sponges remain to be an excellent renewable source of this structural biopolymer due to

their ability to be cultivated under marine farming conditions [19,39]. Recently, unique and ready-to-use nanostructured 3D chitinous scaffolds of sponges (Porifera) origin with interconnected microtubular architecture (Fig.1) [7,10,14–17,20,21,27,30,40–49] have been proposed as highly potential matrices for applications in regenerative medicine and tissue engineering [18,28,50–60], extreme biomimetics [61–68], electrochemistry [69] and environmental science [31,70].

We are the first to present a modern review of poriferan chitin bioarchitecture with respect to 3D morphology. We will discuss the occurrence of corresponding chitinous nano-, micro- and macro-scaffolds in sponges, as well as their structural and physicochemical features.

2. PORIFERAN SKELETONS AS SOURCES OF 3D SCAFFOLDS

Sponges are mostly sessile filtering organisms that possess both micro- and macro-porous 3D structured rigid non-mineralized and mineralised skeletons. The mechanical stability of such constructs is crucial for the survival of sponges, especially as natural constructs. Indeed, sponge skeletons, having been evolutionary approved, allow the appropriative settlements of corresponding cells and tissues, as well as provide the resistance to underwater flow currents [22,30,40,71,72]. Skeletons of calcarean sponges are based on exclusively calcium carbonates; although those of glass sponges can contain both silica [73,74] and calcium carbonates [26,75]. However, diverse representatives of keratosan demosponges, also known as commercial or bath sponges, possess mineral-free proteinaceous skeletons made of structural collagen-like protein spongin (Fig.2) (see for overview [11,76–78]). Nowadays, spongin-based sponges are cultivated worldwide, and, consequently, spongin has a great potential to be used as a renewable biological material that can be produced on a large scale [78]. Due to their excellent thermal stability, 3D spongin scaffolds were used as templates to develop functional composite materials using an extreme biomimetics approach [79–82]. The same biomaterial in the form of scaffolds has been effectively used for the immobilization of selected enzymes [83–85], in tissue engineering [78,86] and as biosorbent [87–91].

Figure 2. Typical example of 3D spongin scaffold isolated from marine demosponge *Hippospongia communis*. This biological material possesses a well-developed surface due to the existence of both micro-and macropores.

Among marine demosponges, only representatives of the Verongiida order are known to synthetize biologically active substances [92,93] and possess skeletons composed of structural polysaccharide chitin. The unique architecture of such chitinous skeletons (Fig.1) opened the window for their recent applications as adsorbents, as well as scaffolds for tissue engineering and biomimetics as mentioned above. The overall goal of future research on chitin-producing demosponges is to monitor both novel specimens within the Verongiida order and other orders, as well as to find novel and alternative sources of naturally prefabricated chitinous scaffolds [42, 45–49], especially in those demosponge species which can be cultivated on a large scale using marine farming techniques.

The overview of chitin-producing sponges including marine and fresh water specimens is represented in Fig.3.

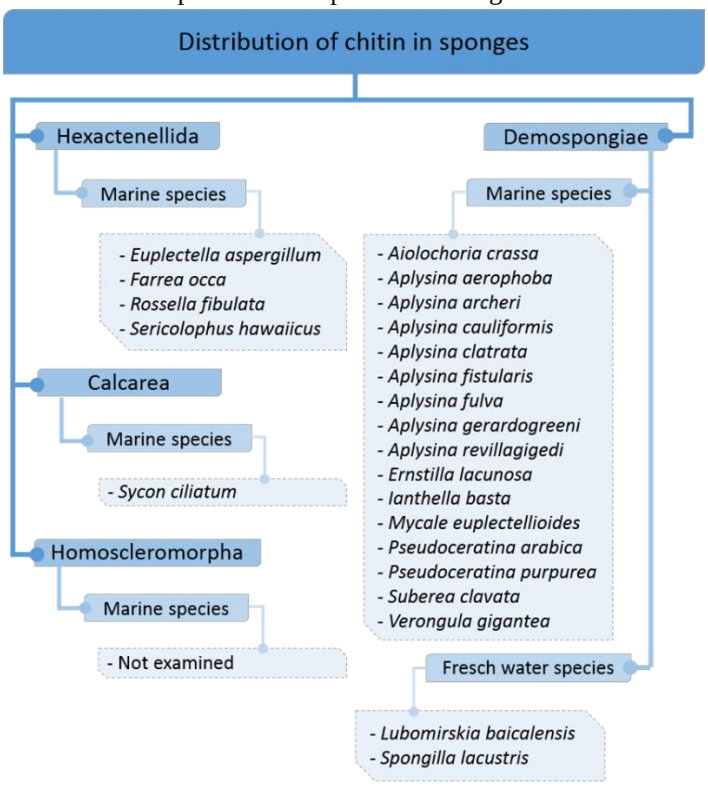

Figure 3. The overview of chitin producing sponges reported from 2007 till 2020.

3. 3D NANOSCAFFOLDS MADE OF SPONGE CHITIN

It is well recognized that chitin, including that of poriferan [94] origin,is represented by nanocrystallites with a diameter of about 2 nm, having been observed numerous times using high resolution electron microscopy (HR-TEM) (Fig. 4). Nanofibrillar architecture of chitin is to be found in skeletal fibres of verongiid sponges and was visualized using scanning electron microscopy (SEM) (Fig.5).

Consequently, the discovery of 3D chitinous nanoscaffold in sponges was not surprising. A unique example of highly ordered nanoorganized chitin (Fig. 6) wasfor the first time foundin siliceous anchoring spicules of glass sponge *Sericolophus hawaiicus* [19], the habitat of which lies near Hawaii Islands at the depth of 600 m.

While investigating glass sponge, the spicules of which were considered as highly ordered silica–chitin composite with

biophotonic properties, Ehrlich and co-workers discovered its ability to generate a supercontinuum of light [95]. The complex process of supercontinuum generation is known to be useful in designing spatially coherent white light sources emitting light simultaneously in the ultraviolet, visible and infrared ranges. Moreover, it should be noted, that artificial fibres showing similar supercontinuum properties are synthetized under high temperature (between 1000°C and 2000°C), whereas glass sponge supercontinuum was generated by an ordered chitin structure which has been naturally synthesized on the sea bed at 4°C [95].

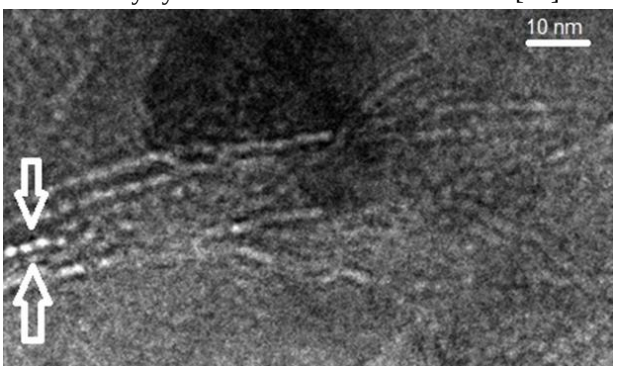

Figure 4. HRTEM image: A bundle of nanofibrils of *Verongula gigantea* sponge chitin with a diameter of 2 nm, which contain typical nanocrystals of chitin (arrows).

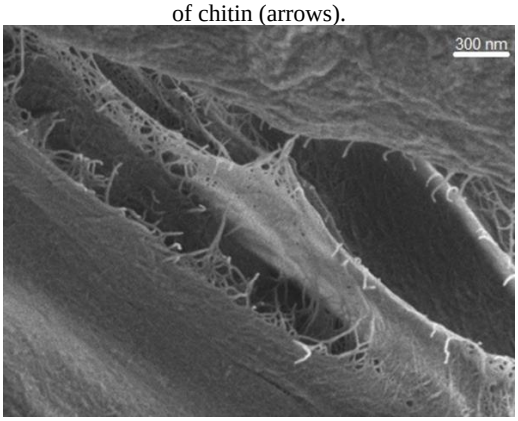

Figure 5. SEM image of the nanofibrils-based network observed within mechanically disrupted chitinous microfibre of *Aplysina fulva* demosponge.

The presence of nanoscaffolds made of chitin has been also observed in experiments with electrochemical deposition of copper and copper oxides on and within microfibers of chitin isolated from marine demosponge *Ianthella basta* [68] (Fig. 7).This raises an intriguing question: is the mechanical integrity of hierarchically structured chitin-based nanocomposites determined by nanostructural organization of the corresponding metallic phase, or does chitin remain to be the main player?

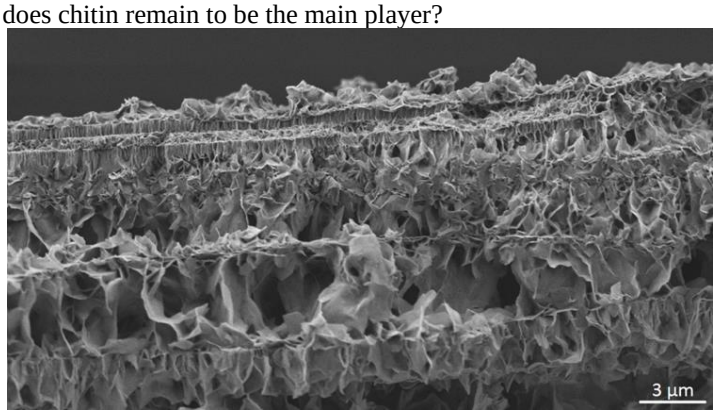

Figure 6. SEM image of highly ordered nanostructured chitin matrix, which becomes visible after desilicification of the *S. hawaiicus* anchoring spicule.

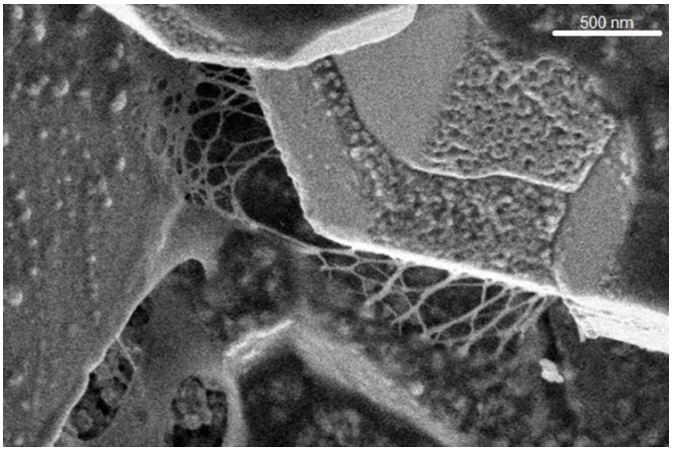

Figure 7. SEM image of Cu and Cu_2O nanocrystals,"arrested" within the nanofibrils of the chitinous nanoscaffold of *I. basta* demosponge origin.

4. 3D MICROSCAFFOLDS MADE OF SPONGE CHITIN

Nanofibrils of chitin in skeletal structures of Verongiida sponges represent the base elements of microfibers, the diameter of which ranges from 50 to 100 µm (Fig.8, 9). The main characteristic features of chitinous microfibers are represented by their tubular architecture and interconnection within cylindroid (Fig.1), or flat (Fig.8) skeletal frameworks, which are species-dependent [11, 43, 96].

The occurrence of microtubular architecture remains crucial for practical applications of such 3D constructs due to capillary forces and corresponding effects. Recently, it was confirmed that chitinous microfibers from *Aplysina archeri* demosponge skeleton possess an excellent capacity for saturation with water, methylene blue dye, blood and crude oil [27]. The swelling capacity of such microfiber-based scaffolds with respect to water was measured at 255 ± 8% [27].

Figure 8. Acellular flat skeletal chitinous scaffold isolated from *I. basta* demosponge.

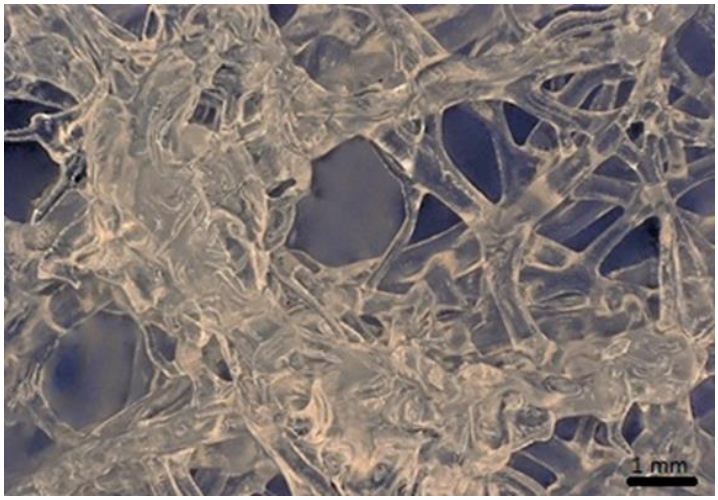

Figure 9. Purified 3D chitinous scaffolds isolated from *I. basta* skeletal framework (see Fig. 8).

The principal schematic overview concerning the ability of sponge chitin to swollen corresponding liquids is represented in Fig. 10. This property allows for the application of chitinous scaffolds isolated from verongiids as 'ready-to-use' capillary system [27] in tissue engineering [31, 50, 51, 56], electrochemistry [69], extreme biomimetics [62, 97, 98] and drug release [58]. Such constructs were suggested to be used for the replacement of damaged skin fragments or as alternatives for wound dressing, including follow-up plastic surgery treatments [57].

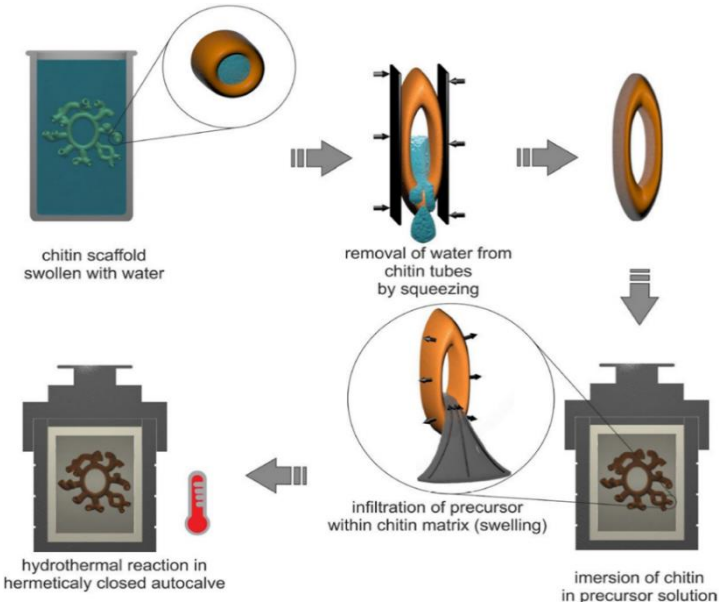

Figure 10. Schematic overview on the principles of "squeezing-swelling" function of chitinous microfibers of poriferan origin.

Nowadays, owing to the wealth of knowledge on sponge chitin, we propose the schematic overview (see Fig.11) showing the potential of naturally pre-designed scaffolding strategies in a wide range of practical applications. Undoubtedly, poriferan chitin proves to be useful in diverse fields of human activity, especially due to the possibility of cultivating of corresponding sponges species using marine aquaculture at depths of up to 3–5 m [19, 39]. The excellent ability of verongiid sponges to regenerate their tissues of up to 12 cm per year [99] remains to be the crucial point in this case. Marine ranching of verongiid sponges as a renewable source of chitin should resolve the supply problem with respect to this highly specialized 3D chitin on a large scale.

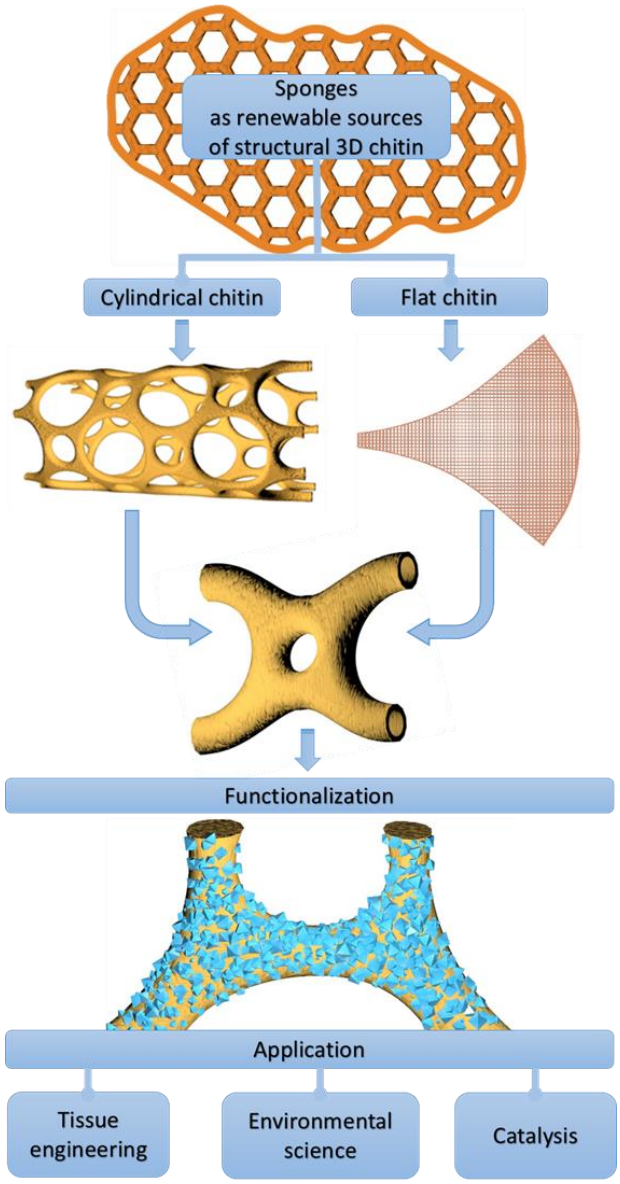

Figure 11. Schematic overview on sponge chitinous scaffolds with respect to their architecture and applications.

It is well recognized that the corresponding microporous 3D constructs of artificial or natural origin can be used in tissue engineering and regenerative medicine. Recently, such types of scaffolds derived from verongiids have been successfully used for tissue engineering of selected human bone marrow-derived mesenchymal stromal cells (hBMSCs), human dermal MSCs [51, 54–56], chondrocytes [18, 50] and cardiomyocytes differentiated from human-induced pluripotent stem cells (iPSC-CMs) [57].

Also, an intriguing methodological approach to obtain calcium carbonate deposition *ex vivo*, using living molluscs hemolymph and 3D scaffold of sponge origin, has been described [60]. Thus, *A. archeri* demosponge and industrially cultivated terrestrial snail *Cornu aspersum*were selected as appropriate 3D chitinous scaffold and as hemolymph donor, respectively. The formation of calcium carbonate mineral phase on the surface of chitinous scaffold after its immersion into isolated snail hemolymph was evidently confirmed. Finally, a new biomimetic product based on *ex vivo* synthetized amorphous calcium carbonate and calcite tightly bound to the surface of chitin was created [28, 60].

Chitin is known as a biological material that can withstand harsh chemical conditions and temperatures of up to 360°C [97]. This property has been recently used for functionalization of the

sponge chitin surface with copper and copper oxide using electroplating [68] (Fig. 12and 13). Due to the large surface area of sponge chitin scaffold it could potentially be used as a heterogeneous catalyst and as a template for the preparation of other complex metaloxide heterogeneous catalysts. Based on Cu/Cu_2O composition catalysts, it could be used in various processes such as cleaning of wastewater from a wide range of organic compounds including dyes [68, 82].

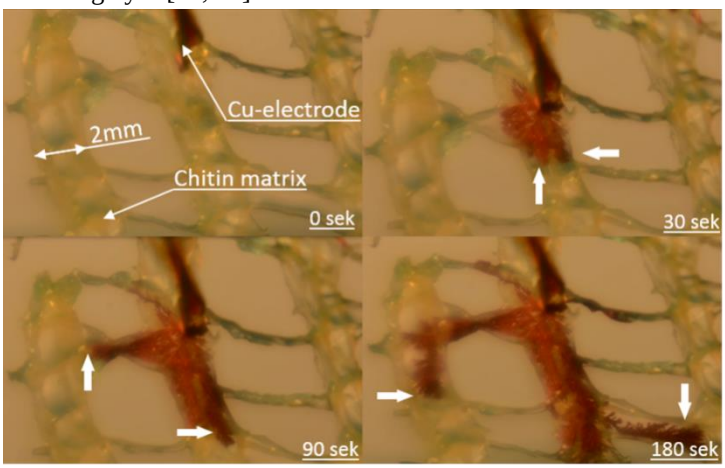

Figure 12. Selected light microscopy images representing the process of copper deposition on and within tube-like chitinous network of *I.basta* demosponge in time. The electrochemical processes should be optimized for these chitinous constructs with respect to current, voltage, and composition of the electrolyte.

This metallization of chitinous scaffolds opens a novel sub-direction within extreme biomimetics [98] to a myriad of straightforward applications in a range of technologies [64,82]. Since the processing of powdered chitin from fungi or industrially harvested crustaceans into sponge-like materials or foams is technologically difficult and expensive, such thermostable chitin-based sponge scaffolds are of potential interest for materials science.

The use of chitin as a biosorbent of diverse heavy metals ions, dyes, crude oil, pesticides, has been reported in numerous papers [100-105], but not with respect to chitin of sponge origin. To the best of our knowledge, there is only one report by Schleuter and co-workers concerning uranium [70]. In this paper, it was shown for the first time that chitin-based scaffolds isolated from *A. aerophoba* demosponge possess the ability to effectively adsorb uranium up to 288 mg/g. Sponge chitin adsorbs uranium from solution with a higher adsorption capacity than many other chitinous sorbents. Moreover, both adsorption and desorption of uranium did not result in any destruction of chitinous scaffolds[70]

Figure 13. Metallization of 3D chitinous matrix isolated from *A. fulva* demospoge using electroplating of copper.

5. 3D MACROSCAFFOLDS MADE OF SPONGE CHITIN

One of the most important advantages of sponge chitin, in contrast to traditionally used chitin sources such as fungi, worms, molluscs and arthropods, is the size of chitin-producing sponges, which can reach up to 1.5 m in diameter (i.e., the elephant ear sponge *I. basta* [99]) or up to 1.5meter in length, which was recently reported by Wysokowski and co-workers [60] for stove-pipe sponge *A. archeri* (Fig. 14).

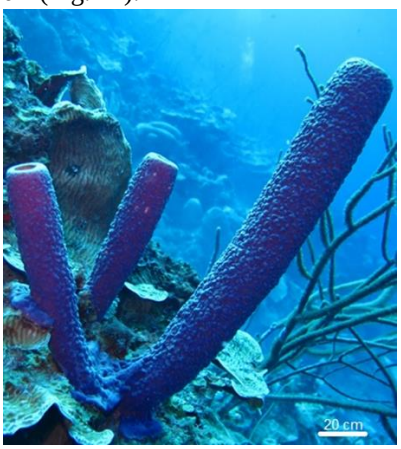

Figure 14. The giant Caribbean stove-pipe sponge *A. archeri*with its up to 1.5-meter-long chitin-based skeletal tubes (of inner diameter ≤10 cm) represents an example of renewable natural source for the isolation of unique tubular chitinous macro-scaffolds to be used in a wide range of applications (see Fig.15).

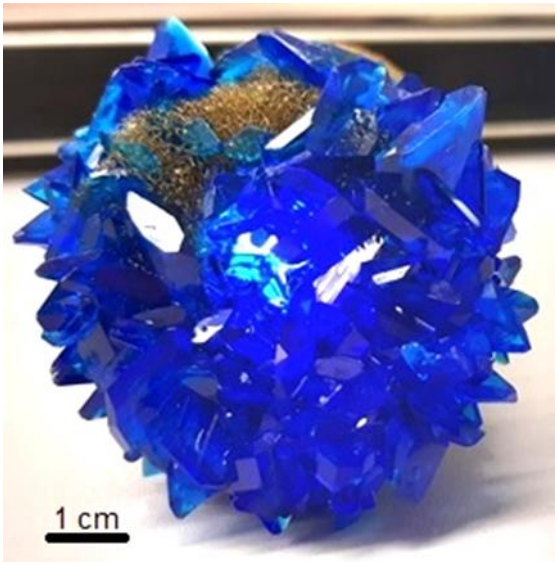

Figure 15. Centimeter-large crystals of copper sulphate synthesized *in vitro*on the surface of tubular chitinous macroscaffold isolated from *A. archeri* demosponge (see Fig. 14).

The skeleton within the tube-like body of *A. archeri* marine sponge represents a unique, naturally pre-fabricated, hierarchically structured fibrous chitin-based macro-construct, which can be up to 150 cm long, with an inner diameter of up to 10 cm. It was

suggested that such chitinous constructs represent the longest known tubular chitin [60]. This unique source of pre-designed microporous chitin has a distinct advantage for the applications in technologies where large crystals of the corresponding inorganic phase can be generated directly on macro-chitin (Fig. 15).

6. CONCLUSIONS

The chitin system in nature is recognized as ancient, being structurally developed through million years of evolution in diverse extinct and extant uni- and multi-cellular organisms. Possible molecular mechanisms of chitin formation and its structural diversity on nano-, micro- and macro-levels are still under investigation. From the viewpoint of applied science, chitins of poriferan origin represent an intriguing scientific field aiming at the global application of such naturally pre-designed constructs as environmentally friendly bioadsorbents against diverse chemical contaminants, as scaffolding chitinous biomaterials for regenerative medicine, including tissue engineering and as 'ready-to-use' matrices in biomimetics and bioinspired materials science. Provided that chitins can be used in various technologies and demosponges can be cultivated under marine farming conditions, these marine invertebrates have a great potential to be used as sources of unique prefabricated scaffolds. Such contsructs would be further applied for the production of mechanically stable centimeter-large metal-containing composites of controlled shape and size with 3D hierarchical structure in industrially relevant quantities. Consequently, metallization of chitinous scaffolds with nanoparticles of such metals as gold, palladium, nickel and cobalt using modern techniques should be conducted in the future.

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