Review Paper:

Biomimetics helping to design advanced environmental adsorbents

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Abstract
There are many examples from the past, especially from the period of rapid industrial development, when as a consequence of harmful emissions in the biosphere, a mass death of the population and all forms of life occurred. Chemical accidents, means of warfare in wars to destroy the enemy, production of energy related to risks of contamination, loss of biodiversity, electromagnetic smog, oil extraction and oil tanker accidents, transport and exhaust gases, climate threats, production of commodities without respecting the legislative environmental standards and the lack of environmental infrastructure, are the most common consequences in today's modern human life and environmental quality.

Biomimetics (or bioinspiration) is one of the most revolutionary scientific fields of the 21st century. It is usually defined as a science which imitates nature and living systems and helps to sustain life on Earth. Due to a better understanding of biological systems, the ability to observe nature, as well as the number of effective nature-inspired solutions to some current technological problems have increased dramatically.

Keywords: Biomimetics, supramolecular chemistry, imitation of nature, environmental pollution, biopolymers.

Introduction
Biomimetics (from the Greek word bios - life and mimesis – imitation) which is applying knowledge from the nature and functional principles of living organisms, belongs currently to the most progressive scientific disciplines of millennium[3,16]. Also supramolecular chemistry, presenting interdisciplinary intersection of physics, biology and traditional chemistry and including progress in self development, contributes to extraordinary expansion of new scientific and technical knowledge for current societal practice. It also implements advanced analytical methods in order to percept the depth of natural laws as the paradigm for further development and molecular "recognition" of matter.

Here the individual entities, comprehensively and hierarchically integrated, are usually not connected through traditional covalent, but most often by dynamic, reversible hydrogen, donor/acceptor or coordination bonds, under stimulation of the external environmental factors, such as spectacular mechanisms in nature with its "par excellence" homeostasis[3,14,16].

This transformation includes self-replication and amplifications, in terms of Darwin's theory the key moments for the life evolution. During the development of bioactive supramolecular substances and substrates, they generated and mutually integrated on combinatorics principles starting from the molecular level.

Based on a deep knowledge of countless functions of biological organisms and of living systems, the mankind is approaching some technological epoch named revolutionary already in 1959 by Richard Feynman, the so-called algorithm coded in DNA "from the bottom up". In other words, the principle of material synthesis from atomic and molecular level to macro- and supramolecular one as well as to the final properties of products such as superhydrophobic, self-cleaning, biocompatible, multi-functional, heat and radiation resistant, anisotropic etc. actually imitating natural processes (Fig. 1).

Modern science imitating biomineralization of nature: Studying biomineralization helps to understand the principles potentially applied in modern material chemistry and also in the synthesis of new environmental adsorbents and materials and protect the environment in order to promote sustainable development[7]. During millions of years, by evolution optimized biomineralization processes, in aquatic media inorganic minerals like silica, carbonate or calcium phosphate, iron oxides and others were produced. They are characterized by an extremely complex hierarchical structure (Fig. 1). This dynamic transformation, taking place on specific places by controlled condensation of inorganic precursors and enzymes, has been synergistically managed by using highly developed biologically and anatomically adapted physico-chemical processes[20,26,28].

Biomineralization in nature is common. It occurs in bacteria, plants, invertebrates but also in vertebrates. For example, silicon is the second most widespread element in the earth's crust and often occurs as soluble orthosilicate in soils and waters, from where it is accessible to animals and plants or seaweed - diatoms (*Diatomae*) and sponges (*Porifera*). At the concentrations of 1–2 mmol/L of silicon and at neutral pH in waters, orthosilicic acid polycondenses while through the formed siloxane bonds, a crystalline or amorphous silicon dioxide is formed.

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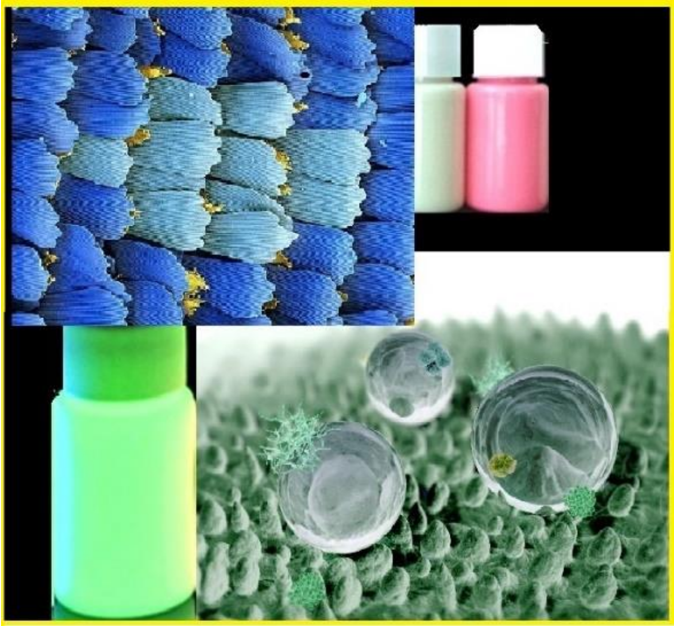

Figure 1: Butterfly wing morphology under the electron microscope (upper) and surface of a lotus leaf graphically adjusted by computer (lower)

Silicon is thus of biogenic origin, however gigaton quantities of this oxide are produced annually by a wider range of living organisms. Unlike traditional procedures and syntheses, natural processes such as growth of mammalian bones or shells seaweeds (*Diatomeae*), therefore, are carried out gradually by creating hierarchically structured organic-inorganic composites, where the so-called soft (organic) substrates organized in nanometer sizes serve as a matrix for controlled growth of specifically oriented and shaped inorganic crystals.

Inorganic phase, formed by precipitation in aquatic media, is oriented towards the so-called domains, controlling soft tissue of the matrix. These biogenic hierarchical composites are characterized by a complex structure with a design that reflects their unique behavior and properties. Furthermore, the soft tissue in their bio - inorganic compartments was formed by evolution in the environment of natural waters. It would ultimately help in the analog biosynthesis of advanced products and will rule out concerns about any environmental pollution, accompanying phenomenon of petrochemical production[5–9].

Another unique example from nature is wavy, almost ace-shaped deformed layers that cover cell walls to fulfill various functions, such as filtering, blocking large molecules and enabling passage of small molecules of excreta during metabolism. These layers with a thickness of about 10 nm are porous, three-dimensional and contain about 30% of the total volume proteins.

The building blocks of proteins that create characteristic periodicity of the layers consist of some regular depressions that could potentially meet function of so-called nucleation centers, when applied by analogically synthesized adsorbents for toxic metals removal[3,14,28].

Microorganisms as nanorobots or the 4th generation of nanoproducts: Living nature is the best inspiration for nanotechnologists because the nature structured all matter and properties of organisms, down to the smallest detail. All taxonomic species in nature contain representatives with biomineralization ability. Until now, there were identified about 60 minerals, biosynthesized in this way[3,17,25,28].

One of the most current examples of biomineralization and its effects on the surrounding environment, that requires an urgent solution, is the production of acid mine waters after ore extraction, in tailings ponds and in mines tunnels.

Numerous environmental burdens with occurrence of aggressive biomineralization are created during the weathering of strongly mineralized deposits of sulfidic minerals the sulfate waters with a high content of accompanying metals (Zn, Cu, Sb, As, Fe, Al, Mn). This process is attributed to the acidophilic chemolithotrophic bacteria *Thiobacillus ferrooxidans* and can be expressed as follows (Fig. 2):

$$FeS_2 + 3.5\ O_2 + H_2O \rightarrow Fe^{2+} + 2\ SO_4^{2-} + 2\ H^+ \qquad \text{pH } 1\text{–}4.6$$

$$Fe^{2+} + 0.25\ O_2 + H^+ \rightarrow Fe^{3+} + 0.5\ H_2O$$

Heavily polluted waters, with extremely low pH, intensively devastate the surrounding environment and threaten the quality of the closed underground and surface waters, therefore, as countermeasures to mitigate their impact, some hydrotechnical solutions, so-called anaerobic ponds, are proposed. Probably, the magnetite (Fe_3O_4) deposits have been also developed by means of magnetotactic bacteria, according to the historical data since Precambrian time, while the self-organization of nanocrystallites has been controlled by magnetosensors[4,8,18,19,27].

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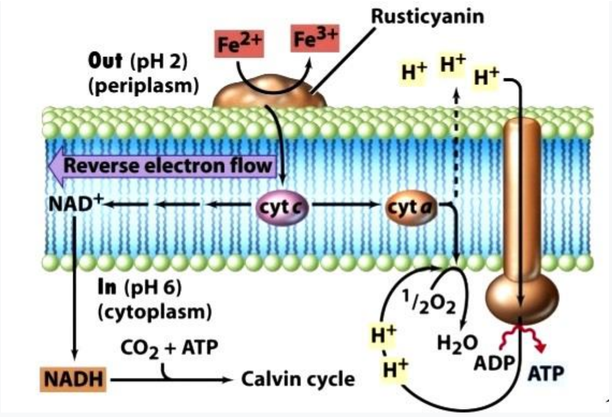

Figure 2: Bacterial iron oxidation by *Thiobacillus ferrooxidans*

There are many examples in nature such as extremophile bacteria from the strain *Deinococcus*-*Thermus (Deinococcus radiodurans)*, in which unique properties were confirmed, such as extremely resistant layers of living cells, protecting them agains external environmental factors, such as acids, increased temperatures, radiation and other degradation factors, that practically irreversibly damage integrity of conventional membranes. So the immobilization of such biomembrane on the external surface of conventional adsorbents would help to stabilize them and significantly increase their added value[8–15]. Polyextremophilic, aerobic, chemo- organoheterotrophic *D. radiodurans* creates multiple copies of its genome and therefore has a unique reparation mechanism.

Some authors justify this unique feature of bacteria based on the presence of Mn(II) complexes, as strong antioxidants, that protect cellular proteins (endonucleases and ligases participating on the DNA reparation mechanism) against radiation, others even by its extraterrestrial origin from Mars, when this bacteria was transported to the Earth with falling meteorites. *D. radiodurans* is also being tried to be genetically modified to be applied for remediation not only of those affected by radiation territories, but also of chemically polluted ones. Current science already masters biochips with thousands of DNA sensors, which can specifically search for specific strings or sections of DNA, controlling a specific physiological function of organisms. As a rule, the hybridization process begins by separating the cells from which the RNA is isolated and generated fluorescently labeled complementary DNA, all done with the help of a computer [1,2,5,9,14,22].

Organisms as natural adsorbents against environmental pollution: There are many examples from the past, especially from the period of rapid industrial development, when as a consequence of harmful emissions in the biosphere, a mass death of the population and all forms of life occurred. Chemical accidents, means of warfare in wars to destroy the enemy, production of energy related to risks of contamination, loss of biodiversity, electromagnetic smog, oil extraction and oil tanker accidents, transport and exhaust gases, climate threats, production of commodities without respecting the legislative environmental standards and the lack of environmental infrastructure, are the most common consequences in today's modern human life and environmental quality[4,18]. The current advanced analytical chemistry is able to identify nano- to picogram quantities of pollutants, the impact of these pollutants on population´s health can not be proven with maximum certainity. It tends to associate with other factors potentially responsible for the current pollution of our environment like immunological, genetic and lifestyle factors. Contemporary analytical chemistry significantly helps to identify pollution in various environmental matrices including tissues of living organisms. That is why the adverse effects of a decade used DDT were proved even in the most remote places on the Earth in fat of polar penguins (*Aptenodytes*), but also human intoxication with toxic metals (plumbism, itai-itai, Minamata, leaded gasoline and others applied for almost a whole century).

Today, the scientific community is trying to simulate these bioaccumulation processes in laboratories and thereby confirming their impact on living organisms or manifesting their significance to neurobehavioral, allergic or endocrine diseases in humans[26-28] . For example, high bioaccumulative ability to pesticides (specifically to DDT) was confirmed using potted plants– groundnut (*Arachis hypogea*), soybean (*Glycine max*), Chinese sunflower (*Sesanum indicum*) and others[5,17,18]. The higher is the natural oil content of these plants, the higher is their ability to bioaccumulate DDT. Also subcutaneous fat of whales and others marine animals (mammals) is rich for persistent organic pollutants (POPs) such as the aforementioned DDT, but also for very common polychlorinated biphenyls (PCBs). Thus today, potential models (biomimetics) for the production of effective POP adsorbents may be invented.

Also specific nanometer-sized substances deposited as membranes or in the form of other structured materials are for cleanup processes prospective, because they have higher adsorption surface and they can be adjusted with a simple incorporating on the carrier. Therefore, development of macromolecular chemistry contributes to the development of ultrafiltration or design of functional membranes such as

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progressive dendritic polymers, discovered in 1979 by Donald Tomalia, which can be relatively easily regenerated only by adjusting the pH of the waters. Perhaps, the only disadvantage currently is its high price[17-20,27].

Current trends in the development of advanced products inspired by nature: Biopolymers or metabolically degradable polymers (agropolymers such as starch, cellulose, chitosan) are object of interest in the last decade due to constant pollution of the environment by fossil fuels, their combustion as well as petrochemical production (Fig.3). Despite these efforts to apply natural resources, biopolymers are currently still expensive compared to petrochemically produced polymers. Moreover, they possess less noble properties in regard to classic synthetic polymers, that is why, they are combined with others natural resources by using new innovative solutions. Typical examples are various nanocomposites, new advanced materials, in which after immobilization, their final properties greatly improve.

The natural clays contribute to the increase of mechanical and hydraulic properties of adsorbents, Fe(0) nanoparticles act to environmental pollutants reductively, titanium dioxide photocatalytically, silver clusters biocidal and magnetite nanoparticles comprehensively, thus in the end result, they increase the chemical functionality of these finals composites[5,8,19,22,27].

Nowadays, biopolymers can be synthesized chemically or by using microorganisms. So far, 4 alternatives are known for that processes: (i) fermentation of agropolymers; (ii) bacterial biosynthesis and extraction of polyhydroxyalcanoates as of naturally degradable polymers, which are very similar to conventional thermoplastics or using gene engineering of modified transgenic plants (*Brassica napus*); (iii) from synthetic degradable polymers such as polylactides (biopolyesters) which are part of renewable resources and are obtained by fermentation of glucose or by condensation from polylactic acids and (iv) primarily from petroleum[4,5,7–9].

Biopolymers are already in the market, based on the low prices of natural biopolyesters. They are manufactured industrially by multinational companies, such as Japanese Mitsui Chemicals, Mitsubishi, Shimadzu, Toyota and Dainippon Ink Chemicals, German Biomer and BASF, the Belgian Galactic-Total, the American Dupont and Monsanto[4,5]. It may be probably only a matter of time, when this trend of industrial production prevail absolutely for numerous commodities.

Conclusion

Nowadays, environmental requirements and the use of renewable energy resources are rapidly asserting, but also constantly increased expenses for manufacturing the conventional adsorbents cause the biomaterials start to be considered as potential adsorbents of the future. In the current literature, objective and critical comparison of adsorption efficiency for environmental adsorbents known so far, is still absent [7,8,20,26]. However, the literature data are not consistent and quite contradictory. New trend for development of advanced natural adsorbents using the bioengineering is irreversible in the world. Despite that, a lot of effort must be done, so that theoretical studies or laboratory experiments move this research into industrial practice.

Biomimetic goods are now considered for the generation of nanoproducts and more than 1000 different ones are already on the market using this principle (sanitary cleaning products, sunscreens and cosmetics, facade self-cleaners coatings and others). Generation of the so-called nanorobots, with the properties of living organisms, is to be understand nowadays only as a science fiction.

Biomimetics (or bioinspiration) is one of the most revolutionary scientific fields of the 21st century. It is usually defined as a science which imitates nature and living systems and helps to sustain life on Earth. Strategies involving molecular recognition, ligand capping, host-guest cluster chemistry and molecular templating are being explored in material chemistry for the construction of high order molecular architectures.

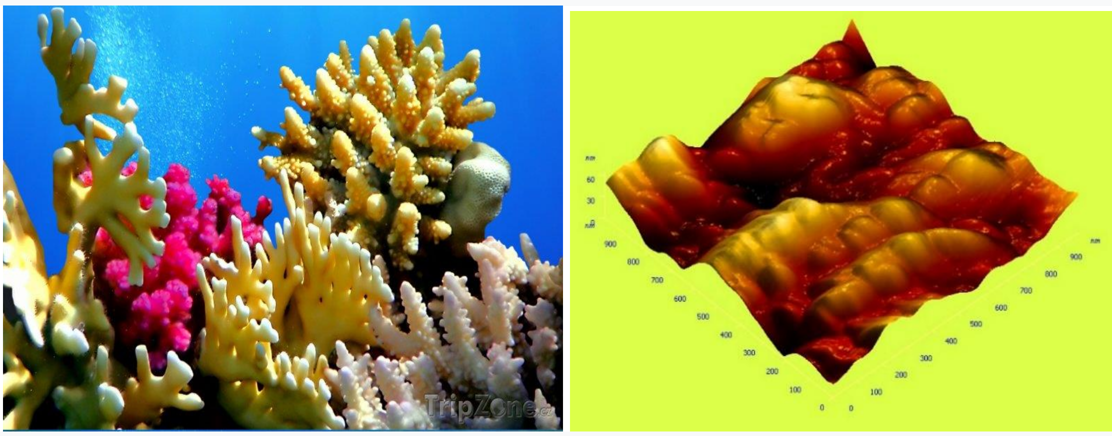

Figure 3: Coral reefs of limestone and siliceous diatoms (left) and chitosan-zeolite composite under STM (right)

The present study reports on several synthetic routes, by which naturally available minerals or even waste products have been combined with specific biogenic components (such as surfactants, alginates and waste polysaccharides) in order to prepare novel functional gradient adsorbents suitable for economically and ecologically viable water decontamination.

References

1. Alexander C., Andersson H.S., Andersson L.I., Ansell R.J. and Kirsch N., Molecular imprinting science and technology: a survey of the literature for the years up to and including 2003, *Journal of Molecular Recognition*, **19**, 106 **(2006)**

2. Boyle R.W. and Jonasson I.R., The geochemistry of antimony and its use as an indicator element in geochemical prospecting, *Journal Geochemical Exploration*, **20**, 223 **(1984)**

3. Behrens P. and Bauerlein E., ed., Handbook of Biomineralization, Biomimetic and Bioinspired Chemistry, Wiley-VCH Verlag, Weinheim **(2007)**

4. Carson R., Silent Spring, Houghton Mifflin Harcourt, Boston **(1962)**

5. Cavrak M., ed., Biomimetic Based Applications, Tech Europe, Rijeka **(2011)**

6. Chil-Sung J., Kitae Baek J.K., Young-Ki O. and Sang Do L., Adsorption of As(III) and As(V) in groundwater by Fe–Mn binary oxide-impregnated granular activated carbon, *Journal Hazardous Materials*, **163**, 804 **(2009)**

7. Chmielewská E., From Not Safe to Environmentally Friendly Processing or Green Chemistry? From History to Present in Development of Zeolitic and Other Industrial Adsorbents, *Current Green Chemistry*, **1(2)**, 108-114 **(2014)**

8. Chmielewská E., Prírodné zdroje na ochranu životného prostredia, Vyd. Univerzity Komenského, Bratislava**,** in Slovak **(2014)**

9. Goto K., Miura T., Hosaka D., Matsumuto H., Mizuno M., Ishida H. and Inazu T., Rapid oligosaccharide synthesis on a fluorous support, *Tetrahedron*, **60**, 8845 **(2004)**

10. Gribbin J. and Gribbin M., Richard Feynman, A Life in Science. Hardcover – July 1, Dutton **(1997)**

11. http://en.wikipedia.org/wiki/Pieter_Harting, copied August **(2015)**

12. Iijima S., Helical microtubules of graphitic carbon, *Nature*, **354**, 56 **(1991)**

13. Jabbari E., ed., Handbook of Biomimetics and Bioinspiration. 1 Bioinspired Materials, World Scientific Series in Nanoscience and Nanotechnology, World Scientific Publishing, Singapore **(2014)**

14. Lehn J.M., Supramolecular chemistry: concepts and perspectives, WCH, New York **(1995)**

15. Meadows D.H., Meadows D.L. and Randers J., Beyond the Limits, Argo, Praha **(1995)**

16. Min J.H. and Hering J.G., Arsenate Sorption by Fe(iii)-Doped Alginate Gels, *Water Research*, **32**, 1544 **(1998)**

17. Mittal V., ed., Advances in Polymer Nanocomposite Technology, Nova Science Publ., New York **(2010)**

18. Oliveira M.B. and Mano J.F., Handbook of Biomimetics and Bioinspiration, Jabbari E., ed., Chapter 7, World Scientific Publishing, Singapore **(2014)**

19. Patrikeev V.V. and Scholin A., Molecular Imprinting Science and Technology: A Survey of the Literature for The Years Up to And Including 2003, Molekuljarnaja Khromatografia, Akad, Nauk USSR Just, Fiz. Khim. 66–72 **(1964)**

20. Polyakov M.V., Synthesis and investigation of xerogels of polysiloxane hydride with various porous structures, *Zh. Fizitscheskaja. Khimija*., **2**, 799 **(1931)**

21. Peng X., Xu F., Zhang W., Wang J., Zeng C., Niu M. and Chmielewská E., Magnetic Fe_3O_4 @ silica-xanthan gum composites for aqueous removal and recovery of Pb^{2+}, *Colloids Surfaces, A Physicochemical and Engineering Aspects*, **443**, 27 **(2014)**

22. Rodriguez-Iznaga I., Petranovskii V. and RodriguezFuentes G., Ion-exchange of amino- and aqua-complexes of nickel and cobalt in natural clinoptilolite, *Journal Environmental Chemical Engineering*, **2**, 1221 **(2014)**

23. Rosabal B.C., Era J.B. and Fuentes G.R., Characterization of Fe^{2+}—containing natural clinoptilolite and its interaction with saccharides, *Microporous Mesoporous Materials*, **38**, 161 **(2000)**

24. Russel W.B., Supramolecular Science, *Journal of Organic Chemistry*, **66**, 6857-6872 **(2001)**

25. Vijaya Y., Srinivasa R.P., Boddu V.M. and Krishnaiah A., Modified chitosan and Calcium alginatebiopolymer sorbents for removal of nickel (II) through Adsorption, *Carbohydrate Polymers*, **72**, 261 **(2008)**

26. Watkins R., Weiss D., Dubbin W., Peel K., Coles B. and Arnold T., Investigations into the kinetics and thermodynamics of Sb (III) adsorption on goethite, *Journal Colloid Interface Scicience*, **303**, 639 **(2006)**

27. Wegner G., Functional Polymers, *Acta Materialia*, **48**, 253 **(2000)**

28. Zhou Y., ed., Bio-Inspired Nanomaterials and Nanotechnology, Nova Biomedical Books, Nova Science Publ., New York **(2010)**.

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