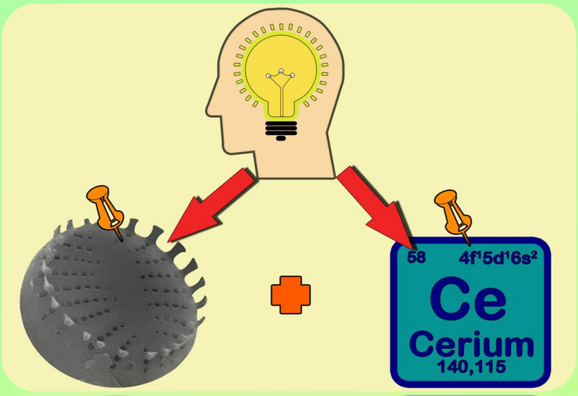
Metabolic insertion of biosilica obtained from diatoms with cerium ions

NICOLAUS COPERNICUS UNIVERSITY IN TORUŃ
Faculty of Chemistry

I. Wojtczak[a], M. Sprynskyy[a], B. Buszewski[ab]

[a] Department of Environmental Chemistry and Bioanalytics, Faculty of Chemistry, Nicolas Copernicus University, 7 Gagarina Str., 87-100 Toruń, Poland, e-mail: izabelawojtczak1991@gmail.com
[b] Centre for Modern Interdisciplinary Technologies, Nicolaus Copernicus University, Wilenska 4 Str., 87-100 Torun, Poland;

Introduction



Graphic concept of the work assumptions

Diatoms are single-celled algae of microscopic size (from 5 µm to 500 µm). They can live singly or form colonies where each cell is a separate entity. The greatest peculiarity and most important feature of diatoms is the structure and composition of the cell wall. Diatom frustules are perforated with periodical pore systems, thus creating unique openwork and three-dimensional structures. The possibilities of 3D structure silica biosynthesis can be extended by chemical modification of diatoms in the process of growth. The synthesis carried out by these microtechnologists and the possibility of adding other elements to their structure, makes it possible to obtain a modern material. Therefore, it seems ideal to combine the unique structure of biosilica with the unique properties of elements from the rare earth group.

Since the 1950s, when the first applications for REE were developed, there has been a constant increase in demand for this group of raw materials. This is due to the discovery of new applications for them. Cerium is used in modern technologies so-called " high-tech". It is used in the production of automotive catalysts, various electronic devices such as phones, tablets and LEDs, as well as in the reduction of nitrogen oxide consumption in catalytic processes.

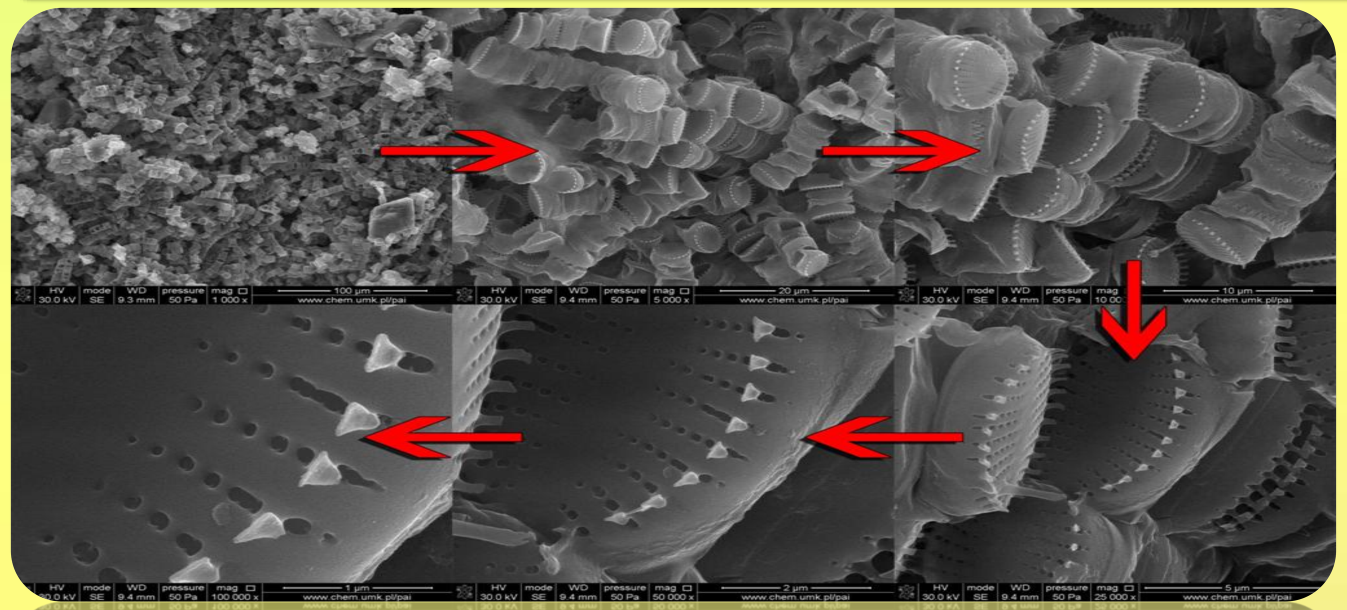
Cultivation of selected species of diatoms in laboratory conditions opens the perspective of controlled biosynthesis of 3D orderly silica structures doped with rare earth metals. The aim of the research work is the synthesis of openwork biosilica with a three-dimensional structure doped with cerium. The realization of this task consists in the cultivation of diatoms of the species *Pseudostaurosira trainorii* under laboratory conditions and *in vivo* admixture of cerium ions when manipulating the culture conditions. Characteristics of morphological and structural features, physicochemical properties, as well as the content and distribution of the admixed element were analyzed after a series of instrumental methods.

Materials and Methods

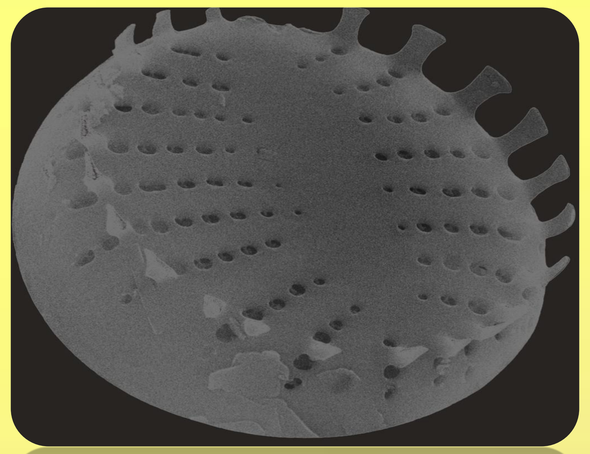
The diatoms of the *Pseudostaurosira trainori* collection of Baltic algae of the Institute of Oceanography at the University of Gdańsk are subject to multiplication. The cultivation is carried out in 2-liter glass flasks, for an average period of 10 to 12 days, with the Guillard F2 culture medium (which is a solution containing trace elements necessary for the proper growth of the culture) and a pH value of 8.2, lighting with 2 fluorescent lamps (1500 lux) at 19-20°C. The concentration of silicon in the culture medium ranged from 7.0 mg/L to about 80 mg/L, and the concentration of cerium was 3.5 mg/L. It is necessary to add the above mentioned culture medium and vitamins such as thiamine, biotin and cyanocobalamin and the required salts: sodium metasilicate, which is a source of silicon, sodium nitrate and sodium dihydrogen phosphate. The next stage of the experiment is adding a compound containing the element with which the diatoms are doped. In the case of currently conducted research, it is ammonium and cerium (IV) nitrate. At the very end, after the previously corrected pH value has been established, an inoculum is added in the form of a solution of unmodified diatoms of the species ***Pseudostaurosira trainori***, taking an addition of 10 ml of inoculum per liter of culture as a whole. It should also be noted that the necessary activities in the conducted experiments are constant control of the pH, measurement of the density, the number of diatom colonies using a densitometer, and monitoring the morphology of the diatom surface using an optical microscope. The obtained material is subjected to a series of instrumental analyzes.

Diatoms cultivation under controlled laboratory conditions

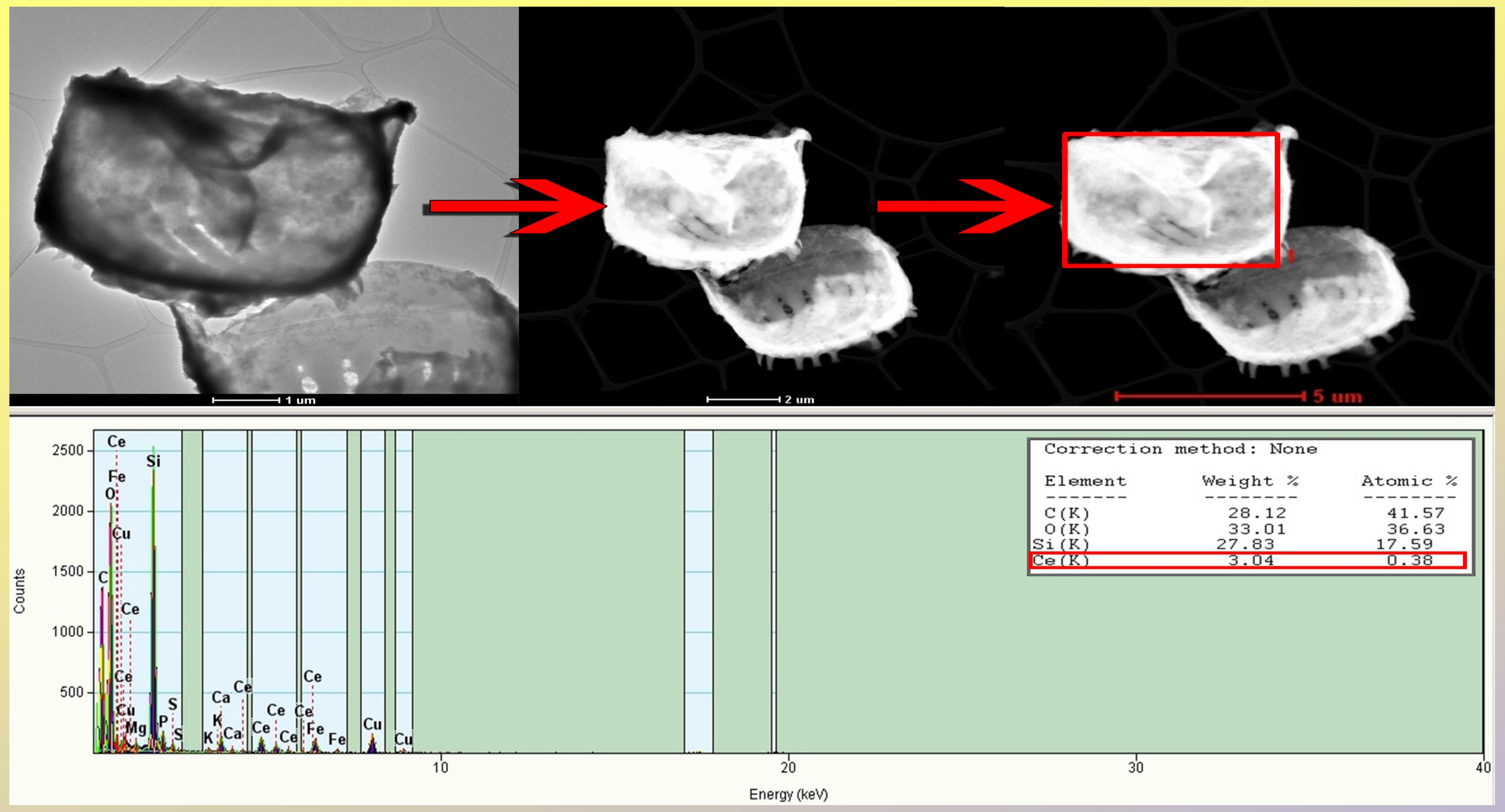
Results



Scanning Electron Microscopy (SEM) images of the diatoms *Pseudostaurosira trainori* doped with cerium ions at different magnification values



Structure of a single diatom cell *Pseudostaurosira trainori*



TEM analysis result for a sample of biomass doped with cerium ions

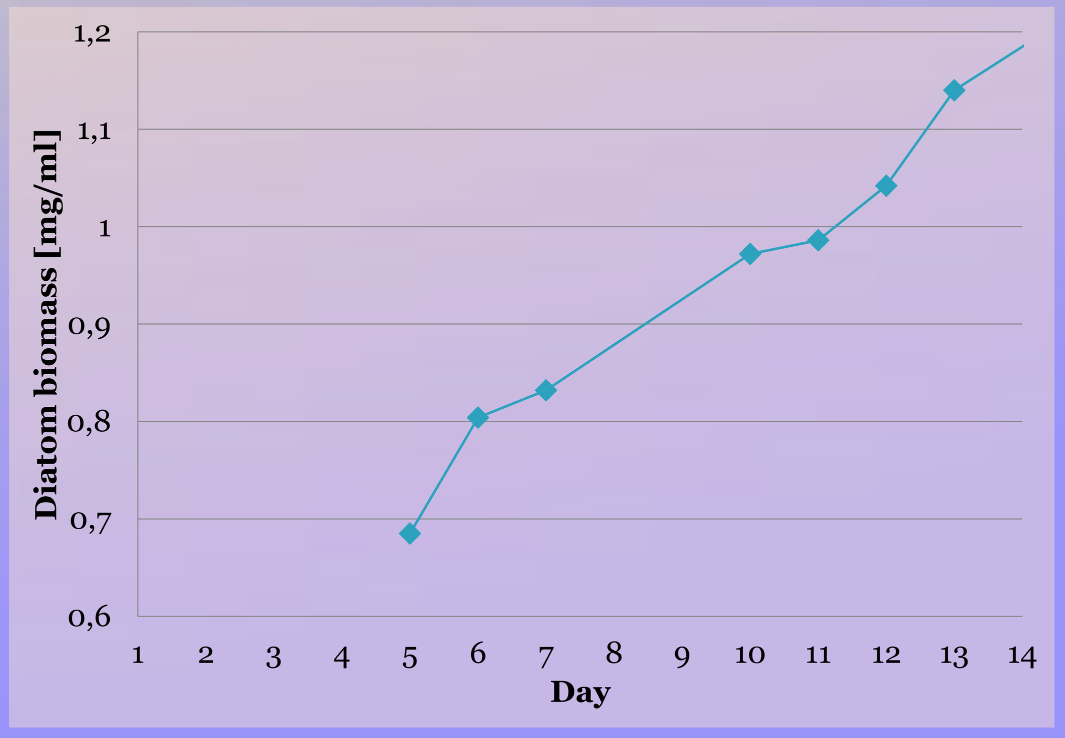
L.p.	Sample name	Cerium concentration in the sample [%]
1	[Ce]=3,5 mg/L pH=7,40 ratio Ce:Si 1:2	1,71
2	[Ce]=3,5 mg/L pH=8,20 ratio Ce:Si 1:2	2,16
3	[Ce]=3,5 mg/L pH=8,95 ratio Ce:Si 1:2	2,87
4	[Ce]=3,5 mg/L pH=8,20 ratio Ce:Si 1:5	1,63
5	[Ce]=3,5 mg/L pH=8,20 ratio Ce:Si 1:10	1,13
6	[Ce]=3,5 mg/L pH=8,20 ratio Ce:Si 1:15	1,29
7	[Ce]=3,5 mg/L pH=8,20 ratio Ce:Si 1:17,5	1,31
8	[Ce]=3,5 mg/L pH=8,20 ratio Ce:Si 1:20	1,79
9	[Ce]=3,5 mg/L pH=8,20 ratio Ce:Si 1:22,5	1,97

The percentage of cerium in the analysed samples

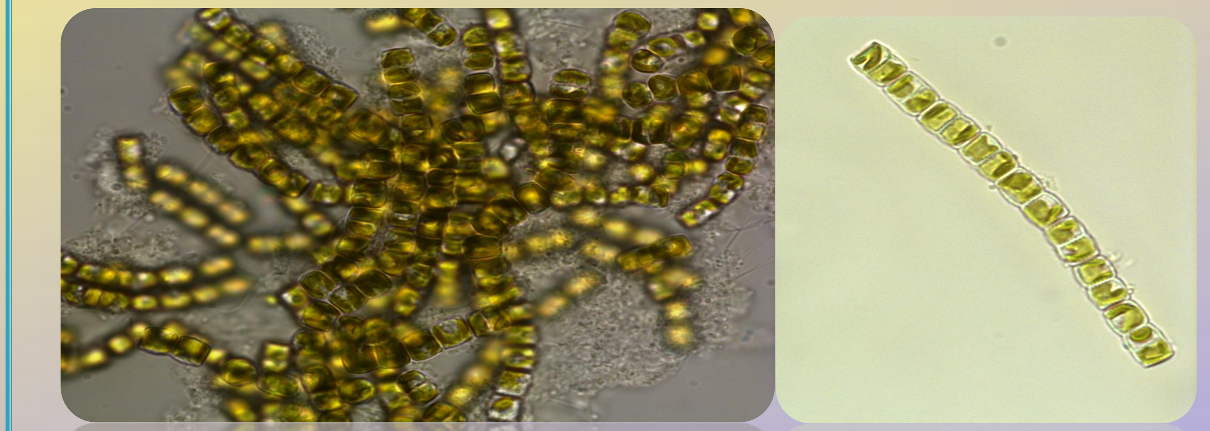
Presented scanning electron microscopy (SEM) images of biomass acquired made of diatoms doped with cerium ions (dried at high temperature), made at different magnification values. It should be noted that the addition of cerium, as a modifying element, did not adversely affect the morphology or structure of diatoms. The cells of diatoms are not affected and no distortions are observed. There are no defects or cracks on the surface, which is an indication of the preserved, natural structure of diatom cells.

The results obtained by TEM (Transmission Electron Microscopy) analysis also prove that the doping diatoms with cerium ions does not affect the deformation of the structure of these microorganisms. Additionally, the result obtained with this method is comparable to the SEM/EDX method described above. The percentage of cerium in the analyzed sample was 3.04%, scanning the whole surface of the sample.

The results presented in the table were obtained using SEM/EDX analysis. The values of the cerium content presented were obtained by scanning the entire surface of the sample. It should be noted that the obtained values of the cerium content in the samples range from 1.13 to 2.87 %. Additionally, it should be noted that increasing the value of the Ce:Si ratio the percentage of cerium in the analysed samples is lower. Moreover, it should be emphasized that the obtained results do not allow to obtain a linear relationship. The character of analyzed variants is variable.



Growth rate of diatoms depending on Ce:Si ratio of 1:5



Photos from the optical microscope of a diatom colony of the species used

The growth kinetics of diatoms were analyzed depending on the variables related to cultivation. During the first experiment the best pH value for the process was determined. Subsequent experiments included analysis of the influence of Ce:Si ratio on culture growth. The values obtained during the experiments allow us to draw conclusions about diatom growth trnds. Namely, during the first days the growth is intense, followed by the days of standstill (about 7-10 days), followed by another growth wave of cultured biomass.

Conclusions

Diatomaceous biosilica is becoming a growing inspiration for many industries, due to its unique properties and a multitude of applications. Expanding this perspective with the possibility of doping diatoms during their growth with one of the representatives of rare earth ions (cerium), allows to obtain an innovative material that can successfully find its application in dynamically developing modern technologies.