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ADSORPTION OF CATIONIC PORPHYRINS BY NANOPARTICLES OF ZEOLITE AND SILVER

A.G. GYULKHANDANYAN

Institute of Biochemistry of NAS RA
anna.g_yan@yahoo.fr

The complexation of cationic porphyrins and metalloporphyrins with nanoparticles of zeolite and nanoparticles of anisotropic silver in aqueous solutions is investigated. Study of porphyrins desorption showed that under the influence of monovalent and divalent salts (NaCl and $CaCl_2$) a complete desorption of porphyrins and metalloporphyrins from silver nanoparticles occurs, whereas from zeolite nanoparticles desorption does not occur.

Cationic porphyrins – zeolite nanoparticles – silver nanoparticles

Ուսումնասիրվել է կատիոնային պորֆիրինների և մետաղապորֆիրինների կոմպլեքսագոյացումը ցեոլիտի և անիզոտրոպ արծաթե նանոմասնիկների հետ ջրային լուծույթներում: Պորֆիրինների դեսորբցիայի հետազոտությունները ցույց տվեցին, որ միավալենտ և երկվալենտ աղերի (NaCl և $CaCl_2$) ազդեցության տակ արծաթե նանոմասնիկներից տեղի է ունենում պորֆիրինների և մետաղապորֆիրինների ամբողջական դեսորբցիա, մինչդեռ ցեոլիտի նանոմասնիկներից դեսորբցիա տեղի չի ունենում:

Կատիոնային պորֆիրիններ – ցեոլիտի նանոմասնիկներ – արծաթե նանոմասնիկներ

Исследовано комплексообразование катионных порфиринов и металлопорфиринов с наночастицами цеолита и анизотропного серебра в водных растворах. Изучение десорбции порфиринов показало, что при действии одновалентных и двухвалентных солей (NaCl и $CaCl_2$) происходит полная десорбция порфиринов и металлопорфиринов с наночастиц серебра, тогда как с наночастиц цеолита десорбции не происходит.

Катионные порфирины – наночастицы цеолита – наночастицы серебра

The search for new methods for photodynamic therapy of cancer (PDT) and the fight against antibiotic-resistant microorganisms is one of actual problems of modern medicine. In both directions, photosensitizers (PS) have been used with high efficiency. In PDT [1] and for photodynamic inactivation of microorganisms (PDI) [2] PS are a widely used as preparations, which selectively accumulates in tumor cells and microorganisms and exposed to light causes irreversible destruction of tumors and bacteria [2].

Currently in Armenia more than 100 new cationic porphyrins and metalloporphyrins are being synthesized [3] (fig. 1) and *in vitro* in the laboratory their high effectiveness against different cancer cell lines, and against different microorganisms were shown [4, 5].

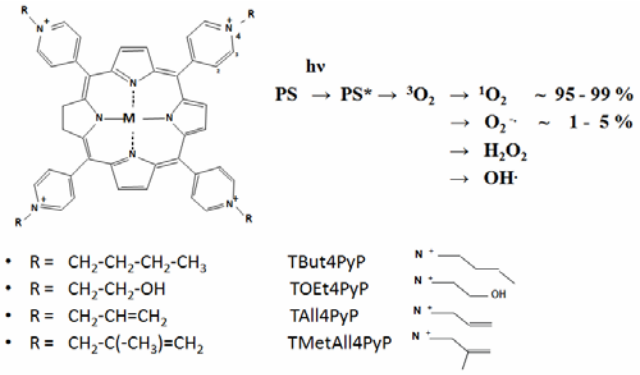

Fig. 1. Cationic porphyrins and metalloporphyrins and the formation of toxic reactive oxygen species. M – the central metal atom in the metalloporphyrins, R – peripheral functional groups.

One of the promising approaches enhance the effectiveness of PDT of tumors and PDI of microorganisms is the use of nanocontainers from nanoparticles of precious metals (gold and silver) [6]. Selection another inorganic nanoplatform of zeolite nanoparticles was due to their special properties. They occupy a special place among other nanoparticles due to the unique sorption capacity and high biological activity.

To enhance the effectiveness and targeted delivery of photosensitizers for PDT of tumors and PDI of microorganisms we used zeolites and anisotropic nanoparticles of silver. For this purpose we studied the adsorption of different cationic porphyrins and metalloporphyrins via zeolite nanoparticles and nanoparticles of anisotropic silver as well as desorption of porphyrins from formed nanocomposites was investigated.

Materials and methods. Study of processes sorption and quantitative description of the binding of porphyrin molecules with the nanoparticles of zeolite and silver was carried out in vitro in the spectral quartz cuvettes on the spectrophotometer "Shimadzu" UV - VIS 2100 (Japan) in the range of 200-800 nm. Anisotropic silver nanoparticles were purchased from "Biovar" Co. Ltd., Yerevan, Armenia.

Zeolite nanoparticles. Nanoparticles of natural zeolite mineral - clinoptilolite of nanometric sizes were obtained by mechanical crushing and subsequent sedimentation in aqueous solution [7]. The size of nanoparticles by laser analyzer type IG-1000 (Shimadzu, Japan), range 0.5 – 200 nm, or electron microscopy was monitored.

Results and Discussion. To study the binding of zeolite of and silver nanoparticles to porphyrins were selected 5 types of cationic porphyrins so that they differed by hydrophobicity (various peripheral groups), by the presence of a hydroxyl group (for studying the possible hydrogen bonding to the surface of the zeolite), by the presence of central metal atom (metal-free and with Zn), by different positions of the side functional group (3rd or 4th position in the pyridyl ring): TOEt4PyP; TBut3PyP; Zn-TOEt4PyP; Zn-TBut3PyP; Zn-TBut4PyP. To achieve the maximum gain of PDT of tumors, as well as PDI of microorganisms under photodynamic action is necessary desorption of porphyrins with nanoparticles.

Since binding of porphyrins as a ligand to nanoparticles in the initial phase of interactions is determined by Brownian motion of porphyrins, from the thermodynamic considerations to be expected that the interaction of porphyrins with nanoparticles can be temperature dependent. Comparison of two temperature modes (18^0C and 37^0C) of the binding the metalloporphyrin Zn-TOEt4PyP, Zn-TBut3PyP and others porphyrins with zeolite nanoparticles by absorption and fluorescence spectroscopy methods showed an

apparent temperature dependence of such a process. Study of the action of monovalent and divalent salts (NaCl and $CaCl_2$) has shown that desorption of porphyrins and metalloporphyrins from formed zeolite nanocomposites does not occur.

Among the many types of nanoparticles-nanocontainers used to enhance the efficiency and for targeted delivery of photosensitizers, anisotropic silver nanoparticles occupy a special place due to a number of rare valuable qualities. We have studied the interaction of silver nanoparticles with the above mentioned cationic porphyrins and Zn-metalloporphyrins and had shown that the formation of nanocomposites is mainly occurs due to the electrostatic interaction between the positively charged groups of porphyrins with the surface of nanoparticles of the anisotropic silver (the binding more than 70%). By absorption and fluorescence spectroscopy is shown that under the action of monovalent and divalent salts (NaCl and $CaCl_2$) comes a complete desorption of porphyrins and metalloporphyrins from silver nanoparticles. Thus, due to this as nanocontainers of photosensitizers anisotropic silver nanoparticles can be much more effective than the zeolite nanoparticles.

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