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ZEOLITE NANOPARTICLES – NANOCONTAINERS OF PORPHYRINS

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The sorption of five cationic porphyrins and metalloporphyrins as well as well-known anionic photosensitizers (chlorin e6 and Al-phthalocyanine) was investigated with zeolite nanoparticles. It is shown that the percentage of adsorption of porphyrins with zeolite nanoparticles is more than 90 and that the predominant mechanism of binding is electrostatic binding of cationic porphyrins with the negatively charged zeolite nanoparticles.

Zeolite nanoparticles – cationic porphyrins – electrostatic binding

Ցեոլիտի նանոմասնիկների հետ ուսումնասիրվել է հինգ կատիոնային պորֆիրինների և մետաղապորֆիրինների, ինչպես նաև հայտնի անիոնային ֆոտոսենսիբիլիզատորների (քլորին e6 և Al-ֆտալոցիանին) սորբցիան: Ցույց է տրվել, որ ադսորբցիայի տոկոսը ցեոլիտի նանոմասնիկների հետ բոլոր պորֆիրինների համար ավելի քան 90 է և որ կապման գերադասող մեխանիզմն է կատիոնային պորֆիրինների էլեկտրոստատիկ կապը բացասական լիցքավորված ցեոլիտի նանոմասնիկների հետ:

Ցեոլիտի նանոմասնիկներ – կատիոնային պորֆիրիններ – էլեկտրոստատիկ կապ

С наночастицами цеолита исследована сорбция пяти катионных порфиринов и металлопорфиринов, а также известных анионных фотосенсибилизаторов (хлорин е6 и Al-фталоцианин). Показано, что процент адсорбции для всех порфиринов с наночастицпми цеолита более 90 и что преобладающим механизмом связывания является электростатическое связывание катионных порфиринов с отрицательно заряженными наночастицами цеолита.

Наночастицы цеолита – катионные порфирины – электростатическое связывание

Currently, photodynamic inactivation of microorganisms by photosensitizers is one of the most promising areas for the destruction of the antibiotic resistant microorganisms [1-3]. Photosensitizers (PS), mainly porphyrins, under action of light promote generation of reactive oxygen species [4], which effectively inhibit growth and kill microorganisms [1-3]. In recent years in order to improve efficiency of porphyrins against microorganisms actively used nanocontainers [5]. Among the many types of nanoparticles-nanocontainers used to enhance the effectiveness and targeted delivery of photosensitizers, nanoparticles of zeolites occupy a special place due to the high biological activity, and unique sorption possibilities of microorganisms [6], as well of ligands - porphyrins [7]. The above presented background of use of zeolites and their advantages are strong argument of the need for detailed and careful study of porphyrin complexes with nanoparticles of zeolite. These tasks of interaction of various cationic porphyrins and zeolite nanoparticles comprise the aim of the present work.

Materials and methods. Study of processes sorption and quantitative description of the binding of porphyrin molecules with the zeolite nanoparticles 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.

Porphyrins and metalloporphyrins. Photosensitizers – water-soluble porphyrins with various side-chain substituents and the central metal atom were synthesized at the Department of Organic Chemistry, Yerevan State Medical University [8, 9] and have been provided for researches. For investigation of sorption on/in nanoparticles of zeolite the following five cationic porphyrins and metalloporphyrins we used: i) meso-tetra (4-N-oxyethyl pyridyl) porphyrin (TOEt4PyP), ii) Zn-TOEt4PyP, iii) meso-tetra (3-N-oxyethyl pyridyl) porphyrin (TOEt3PyP), iv) Zn-meso-tetra (4-N-butyl pyridyl) porphyrin (Zn-TBut4PyP) and v) Ag-TBut4PyP, as well as known anionic photo-sensitizers: chlorin e6 and Al-phthalocyanine.

Zeolite nanoparticles. Nanoparticles of natural zeolite mineral – clinoptilolite of nanometric sizes were obtained by mechanical crushing and subsequent sedimentation in aqueous solution [10]. The size of nanoparticles by laser analyzer type IG-1000 (Shimadzu, Japan), range 0.5-200 nm, or electron microscopy was monitored.

Statistical analysis. The statistical parameters (average values, standard deviation) used in the experiments were calculated using the program Excel.

Results and Discussion. To the solution of porphyrin with volume 2 ml and the final concentration of 10^{-5} M successively 0.2, 0.3, 0.5, 0.6, 0.7 and 0.8 ml of zeolite nanoparticles was added (initial concentration of 0.66 mg/ml). By successively increasing of concentrations of the added zeolite nanoparticles (from 0.2 ml = 0.06 mg/ml to 0.6 ml = 0.15 mg/ml) into a solution of metalloporphyrin Zn-TBut4PyP was shown directly proportional dependence of the increase of its sorption ability (first 4 points on fig.1), whereas adding nanoparticles 0.7 ml = 0.17 mg/ml and 0.8 ml = 0.19 mg/ml saturation of adsorption ability of zeolite occurs (fig. 1).

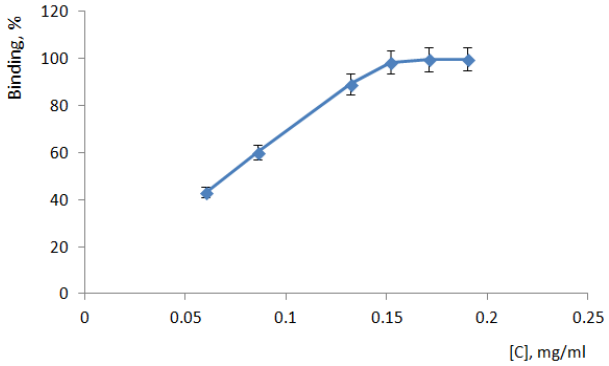

Fig. 1. Percent of binding of metalloporphyrin Zn-TBut4PyP at various concentrations of zeolite nanoparticles in solution

Thus the addition to a solution of porphyrin of zeolite nanoparticles can be carried out to a concentration of 0.15 mg/mL (addition of 0.6 ml zeolite nanoparticles from the stock solution with the zeolite concentration 0.66 mg/ml). Based on the obtained results for all other cationic porphyrins to 2 ml solution of a porphyrin 0.6 mL zeolite was added so that the final concentration of the porphyrin is in solution 10^{-5} M and then counted the sorption after centrifugation of this solution (15 thousand rpm, 15 min) and determining the residual porphyrin (Soret absorption band at 420-440 nm). The results of the sorption by zeolite nanoparticles of 5 different cationic porphyrins as well as the anionic porphyrin chlorin e6 and neutral photosensitizer Al-phthalocyanine are shown in tab. 1.

Table 1. % sorption of porphyrins (10^{-5} M) by adding to a solution of 0.6 ml of zeolite nanoparticles (0.15 mg/ml)

Porphy-rins	TOEt4PyP	TOEt3PyP	Zn-TOEt4PyP	Zn-TBut4PyP	Ag-TBut4PyP	chlorin e_6	Al-phthalo-cyanine
% sorption	97.1 ±3.6%	98.5 ±3.9%	98.3 ±3.9%	98.7 ±4.0%	95.0 ±3.4%	24.4 ±1.1%	0%

Analysis of the dynamics of change in the absorption spectra for porphyrins and metalloporphyrins (10^{-5} M) by adding of nanoparticles leads to the conclusions: i) that the percentage of adsorption on nanoparticles is for all cationic porphyrins more than 90 %, ii) that the predominant mechanism of binding is the electrostatic binding of cationic porphyrins and metalloporphyrins (charge +4) on the negatively charged surface or internal cavities of the zeolite nanoparticles.

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