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SCIENTIFIC CENTER OF POLISH ACADEMY
OF SCIENCES IN KYIV**

**II Ukrainian-Polish
scientific conference**

**Membrane
and Sorption
Processes and
Technologies**

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This II Ukrainian-Polish scientific conference is devoted to the problems in the field of membrane and sorption technologies, their fundamental, applied and industrial aspects, is aimed at international integration of science and education, forming cooperation between universities and research institutions.

Scholars, students and other representatives from scientific, educational and industrial institutions are invited to take part in the conference. The conference will include oral presentations and posters. Additionally, leading experts and scientists in the area of membrane and sorption technologies will present the plenary sections.

TOPICS

Scientific program of the conference includes:

membrane and sorption processes: baromembrane processes; electromembrane processes; membrane gas separation; membrane distillation and pervaporation; novel and non-traditional membrane processes; sorption processes and sorption from liquids and gases; biosorption; hybrid membrane-sorption processes and technologies; nanotechnologies in membrane materials and processes; fuel cells and batteries; membrane contactors; membrane reactors; membrane spacers;

membrane and sorption applications: membrane materials for medical application; membrane materials for alternative energy sources; membrane technology in food industry; membrane bioreactor; water purification; wastewater treatment;

membrane and sorption development: polymeric and inorganic membranes: formation, structure, properties; sorbents: preparation, structure, properties; nanocomposite membranes; electrochemical membrane processes; tissue engineering.

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and the fact that most of the areas of fruit trees Ukraine (75%) are apples, our research has focused on studying the technology of concentrated fruit juices using membrane distillation.

ADSORPTION OF Zn^{2+} IONS BY ALGINATE-HYDROXYAPATITE MICROSPHERES

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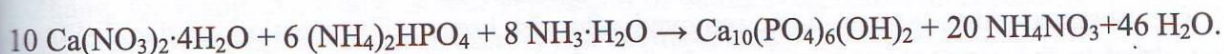
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The significant problem all over the world is bone defects regeneration [1]. A great amount of materials based on hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ (HAp) is used for bone substitution, because it is the main mineral component of bone tissue with excellent adsorption properties [2]. Among them are hydroxyapatite microspheres that can be loaded by growth factors and proteins [3], various drugs [4], antibacterial components [5] for controlled release of such components.

Sodium alginate (AlgNa) is a linear anionic polysaccharide containing of glycoside residuals of α -D-glucuronic and β -D-mannuronic acids. Microspheres are formed due to the gelation of alginate and its crosslinking in the presence of divalent cations (Ca^{2+} , Zn^{2+} , Cu^{2+} etc.) [6]. Zn^{2+} ions are added to the obtained HAp-Alg not only for gelation, but because they have an antibacterial properties and are necessary for bone tissue metabolism. Besides, they have also the stimulatory effect on bone formation, increase bone density and prevent bone loss [7].

Hydroxyapatite is synthesized by following reaction:



As-prepared HAp is mixed in relation 1:1 with aqueous solutions of 1 % AlgNa (sample 1) and 1.5% AlgNa (sample 2) to obtain composite microspheres with w% of AlgNa 0.5 % and 0.75% respectively. The obtained mixtures of HAp were added drop by drop to 0.1 M $CaCl_2$ solution for microspheres formation with AlgCa shell. An experimental setup for HAp-Alg microspheres production is shown in the Fig. 1. Part of obtained microspheres was triple washed by distilled water with following immersion into 0.1 M $ZnSO_4$ for 24 hours (1h, 2h). Another part was remained in 0.1 M $CaCl_2$ (1b, 2b) for 24 hours.

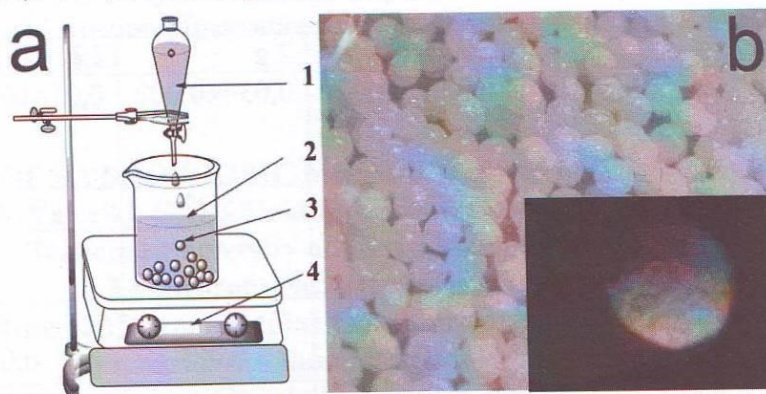


Fig. 1. a) Experimental setup for HAp-Alg microspheres formation: 1) solution of alginate mixed with as-prepared HAp, 2) 0.1 M $CaCl_2$ solution, 3) formation of HAp-Alg microspheres, 4) magnetic stirrer; b) general view of obtained spheres HAp-Alg dropped into 0.1 M solution of $CaCl_2$ (1b) and optical morphology of obtained granules.

The method of formation HAp-Alg microspheres by dropping into 0.1 M ZnSO₄ was also used due to the formation of AlgZn shell with following aging in this solution for 24 hours (1g, 2g).

Morphology of obtained microspheres was investigated by using of optical microscopy (Carl Zeiss) and Scanning Electron Microscopy (SEM) (REMMA-102, SELMI, Ukraine). Phase composition of obtained microspheres was estimated by using XRD (DRON-4, Bourevestnik, Russia) and card catalog JCPDS (Joint Committee on Powder Diffraction Standards). It was shown that phase composition of obtained microspheres is represented by HAp and amorphous alginate. The concentrations of Zn²⁺ were estimated by Atomic Adsorption Spectroscopy (AAS) KAS-120.1 (SELMI, Ukraine) with electrothermal atomization and by titration with ethylene diamine tetraacetate (EDTA).

After finishing of adsorption and desorption processes solution was separated from the solid phase by filtration with paper filter. The concentration of Zn²⁺ ions in the filtrate was determined due to their complex formation with EDTA, which is polydentate ligand that forms complexes with Zn²⁺ in relation 1:1. Eriochrome black was used as indicator, because it also form complex with Zn²⁺ ions which is more stable than Zn-EDTA. Titration was provided in alkaline medium with use of ammonium buffer solution at pH=10 and addition of small amount of indicator which should be completely dissolved. After that titration with EDTA solution is provided up to the color change of investigated solution from wine-red to blue.

Adsorption value was calculated by following equation:

$$A = \frac{(C_0 - C) \cdot V \cdot m_{eqZn^{2+}} \cdot 1000}{m_{microspheres}}, \quad (1)$$

where C₀ is the initial concentration of adsorbate in mol·eq·L⁻¹; C is a equilibrium concentration of adsorbate in mol·eq·L⁻¹; V is an adsorbate solution volume in L; m_{eq,Zn²⁺} – mass equivalent of Zn in g mol·eq; m – weight of microspheres in g, A – adsorption value, mg·g⁻¹ [8].

The obtained microspheres were removed after 24 hours of immersion in the ZnSO₄ 0.2 N solution, dried to the constant mass and weight for calculation of adsorption value of Zn²⁺ ions to dry weight (eq. 1). After that microspheres loaded with Zn²⁺ were immersed into 0.9 % NaCl solution for investigation of their desorption ability. Experiments were provided without mixing at 20°C and ratio of solid to liquid phase - 10:1. Filtrate probes were taken after every hour till four hours. The obtained results are presented in the table 1.

Table 1 – Sorption properties of obtained microspheres.

	1 g	2 g	1 h	2 h	
Concentration of Zn ²⁺ ions in filtrate obtained from AAS data, C _N (Zn ²⁺), mol·L ⁻¹	0,038±0,002	0,034±0,002	0,018±0,003	0,010±0,001	
Adsorption values for dry microspheres after 24 hours of immersion, mg·g ⁻¹	52,40	75,27	77,66	49,28	
Desorption values, mg·g ⁻¹	Desorption time				
	2 hours	0,05	0,08	0,08	0,03
	4 hours	0,09	0,15	0,15	0,05
	6 hours	0,12	0,21	0,21	0,07

For microspheres that were obtained directly in 0.2 N solution of ZnSO₄ after aging in this solution for 24 hours (2 g), the concentration of Zn²⁺ ions in filtrate solution is considerably higher than that for microspheres, obtained in 0.2 N solution of CaCl₂ with following immersion for 24 hour into 0.2 N

tion of $ZnSO_4$ (2h). It could be explained by ability of sodium alginate to additional bonding with ions and formation of Zn-alginate within 24 hours. Besides, with increased concentration of sodium alginate the concentration of adsorbed Zn^{2+} ions and adsorption value are also increased (2h).

The most adsorption values are observed for samples 1h and 2 g. In the case of 1 h it can be explained by the fact that this sample has less weight concentration of Alg (0.5%) than the sample 2 h (5%). The shell of 1h sample has less thickness and let the ions pass through it freely and adsorb by sodium alginate, in this case, bonds only with a proper amount of Zn^{2+} ions that caused by limited amount of active centres ($-COO^-$ - groups) in its molecules. Besides, Zn atomic radius is smaller than Ca is why it is bonded with alginate more effectively. In the samples 1g and 2 g part of active centers are occupied with Zn^{2+} ions at the moment of microspheres formation. After immersion of microspheres into 0.2 solution of $ZnSO_4$ for 24 hours, Zn^{2+} ions are adsorbed by hydroxyapatite as well as by alginate molecules. Adsorption values are increased with increasing concentration of polymer in microspheres (2g).

It was shown from the results of Zn^{2+} ions desorption that they have inverse relationship. Samples with the biggest adsorption values have the biggest desorption values (1h, 2 g). Meanwhile, the maximum release of Zn^{2+} ions is observed after 2 hours. The process of desorption is decreased in time because ion release is occurred from intrinsic layers of microspheres. It is very important for creation of biomaterials for prolonged release of antibacterial components.

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PREPARATION OF HYDROPHOBIC MEMBRANES FOR MEMBRANE DISTILLATION

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Membrane distillation (MD) is a promising technology for desalting highly saline waters. In MD process, vapor pressure difference across the non-wetted porous hydrophobic membranes is the driving force for mass transfer. Different MD configurations including direct contact membrane distillation (DCMD), sweep-gas membrane distillation (SGMD), vacuum membrane distillation (VMD), and air gap