V.I. Vernadskii Institute
of General and Inorganic Chemistry
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MEMBRANE AND SORPTION MATERIALS AND TECHNOLOGIES: PRESENT AND FUTURE

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CHAPTER 16

SORPTION PROPERTIES OF HYDROXYAPATITE-BASED COMPOSITES IN ALGINATE SHELL

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Abstract. *Hydroxyapatite-based composite materials are widely used for treatment of bone defects due to their biocompatibility and osteoconductivity. In this work they were successfully combined with alginate – biopolymer with gel forming ability. Sorption properties of the composite materials towards Cu^{2+} and Zn^{2+} ions were compared. It was shown that sorption of Zn^{2+} ions is more effective due to ion exchange properties and formation of new insoluble phase after contact with microsphere surface.*

Keywords: *hydroxyapatite, sorption, alginate, composite.*

Introduction. Millions of people all over the world suffer from bone injuries and orthopedic problems. They usually need total or partial replacement of the bone tissue [1]. Composite materials based on calcium phosphates and biopolymers are widely used for bone replacement [2]. Hydroxyapatite (HA) ($Ca_{10}(PO_4)_6(OH)_2$) is widely applied as a biomaterial to the substitution of human bone tissues due to its excellent biocompatibility and bioactivity [3].

Polysaccharides perform different physiological functions and have various applications for regenerative medicine and tissue engineering [4]. Polysaccharides are generally more stable than nucleic acids and proteins and are usually not irreversibly denatured on heating [5]. Alginate (Alg) is natural polysaccharide extracted from algae, linear polymer consisting of (1→4) α-L-guluronic (G) and (1→4) β-D-mannuronic acid blocks (M). Alginate found several applications in tissue repair and regeneration, in particular, as a bulking agent, for drug delivery, as a carrier for cell therapies, and as a model of extracellular matrix [6]. Alginates are widely used due to their ability to form beads, films, fibers, hydrogels and composite materials. Divalent metal ions better interact with zones rich in G-blocks comparing with zones rich in M-blocks and MG-blocks [7]. Nanocomposite beads (Alg/HA) are used as drug-controlled release matrices [8]. HA is an ideal material for the preparation of drug scaffolds because of its excellent properties, such as the ability to adsorb a variety of chemical species and biocompatibility. The release of drugs from HA is very fast, owing to the weak interaction between the drugs and the HA particles [9]. The combination of biopolymer and HA seems to be a feasible way to prolong the release of drugs to make the biopolymer/HA composites applicable for long-term controlled release carriers. In this work sorption ability of HA/Alg composite materials to Cu^{2+} and Zn^{2+} ions were compared. \

Experimental. Hydroxyapatite is synthesized by following reaction:

$$10\ Ca(NO_3)_2{\cdot}4H_2O + 6\ (NH_4)_2HPO_4 + 8\ NH_3{\cdot}H_2O \rightarrow \\ \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 20NH_4NO_3 + 46\ H_2O. \qquad (16.1)$$

As-prepared HA is mixed in a relation of 1:1 with aqueous solutions of 1.5% sodium alginate to obtain microspheres with alginate concentration of 0.75%. The mixture of HA/Alg was added drop by drop to 0.1 M $CaCl_2$ solution for microspheres formation with calcium alginate shell. An experimental setup for HA/Alg microspheres production is shown in Figure 16.1.

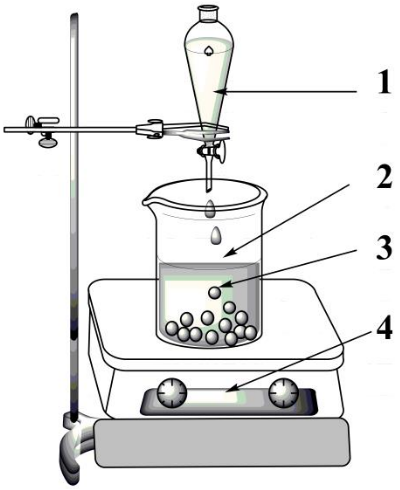

Fig. 16.1. *Experimental setup for HA/Alg microspheres formation: 1) solution of alginate mixed with as-prepared HA, 2) 0.1 M $CaCl_2$ solution, 3) formation of HA/Alg microspheres, 4) magnetic stirrer [10]*

A part of microspheres was triple washed with distilled water followed by immersion with 0.2 N $ZnSO_4$ solution for 24 hours. Another part was immersed with 0.2 N $CuSO_4$ solution. The obtained microspheres were removed after 24 hours from the solutions, dried down to constant mass and weight for calculation of adsorption value of Me^{2+} ions in the dry weight.

The concentration of Me^+ ions in the filtrate was determined via their complex formation with ethylene diamine tetraacetate (EDTA). This is polydentate ligand that forms complexes with Me^{2+} in a relation of 1:1. Eriochrome black (for Zn^{2+}), and murexide (for Cu^{2+}) were used as indicators, because they also form complexes with Me^{2+} ions. Titration was provided in alkaline medium using ammonium buffer solution at pH 10. A small amount of indicator was added. The titration was performed before changing the color of investigated solution.

Adsorption value was calculated by following equation:

$$A = \frac{(C_0 - C) \cdot V \cdot m_{eqMe^{2+}} \cdot 1000}{m_{microspheres}}, \qquad (16.2)$$

where C_0 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; $m_{eq.Me2+}$ – mass equivalent of Me in 1 g (mol-eq); m – weight of microspheres in g, A – adsorption capacity, mg·g^{-1} [11].

Morphology of obtained microspheres was investigated using a Scanning Electron Microscopy (SEM) (REM-106, SELMI, Ukraine). The phase composition of the coatings was examined using an X-ray diffractometer DRON-4-07 (“Burevestnik”, Russia) connected to a computer-aided system for the experiment control and data processing. Phase identification was performed using a JCPDS card catalog (Joint Committee on Powder Diffraction Standards).

Results and discussion. Surface morphology and phase composition is presented in Figure 16.2.

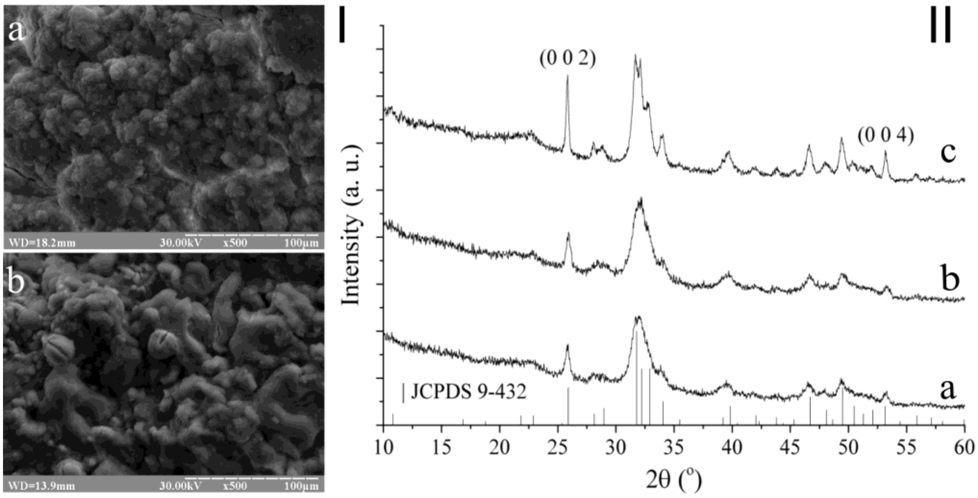

Fig. 16.2. *I) Morphology of Zn^{2+} loaded (a) and Cu^{2+} loaded microspheres (b). II) XRD patterns of a) Zn^{2+} loaded HA, b) Cu^{2+} loaded HA, c) pure HA.*

The microspheres have very developed surface that promote adsorption by HA. The main phase in the microspheres is HA (Figure 16.2. II). Calcium alginate shell of samples permits the passage of ions, further they are adsorbed by HA. To characterize the adsorption capacity, the graphical dependence of adsorption (at 22° C) on contact time is plotted in Figure 16.3.

For understanding sorption mechanism of Zn^{2+} and Cu^{2+} ions on HA/Alg microspheres, solutions of $ZnSO_4$ and $CuSO_4$ with initial concentration of 0.1 M were analyzed to estimate not only amount of mentioned ions, but also Ca^{2+} concentration and pH of the media after contact with adsorbents [10, 12].

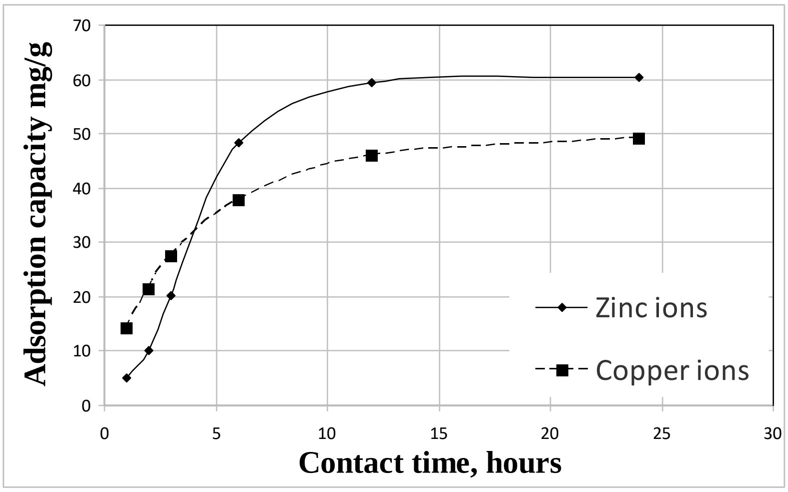

Fig. 16.3. *Adsorption capacity of HA/Alg composite materials.*

The obtained results show mixed character of adsorption. Analysis of filtrate after adsorption of Zn^{2+} and Cu^{2+} ions shows the presence of Ca^{2+} ions in amount of 1/4 from Zn^{2+} ions and 1/3 from Cu^{2+} ions due to ion exchange that accompanies adsorption. The possible substitution of surface cations is due to replacement of Ca^{2+} by Zn^{2+} or Cu^{2+} ions in hydroxyapatite structure. The difference between sorption of ions is caused by ability of metal ions to be embedded to crystal lattice of HA sorbent and formation of insoluble compounds with the HA surface. Product solubility of copper (II) orthophosphate $Cu_3(PO_4)_2$ is $1.3 \cdot 10^{-37}$, while it is $1.0 \cdot 10^{-32}$ for zinc orthophosphate $Zn_3(PO_4)_2$. The difference in solubility product of the phases on the HA surface leads to more intensive adsorption for Cu^{2+} ions at the first hours that is caused by lower solubility product of copper (II) orthophosphate. Besides, the fast formation of insoluble phases leads to blocking of adsorbent active centers with copper (II) orthophosphate with the decrease of adsorption. As a result, adsorption capacity of HA towards Cu^{2+} ions is slightly lower comparing with Zn^{2+} ions.

Conclusions. HA and HA/Alg materials can be used as excellent low-cost natural adsorbents. According to the results of adsorption kinetics, HA has the main contribution to adsorption by HA/Alg composites. Therefore, the mechanism of Cu^{2+} and Zn^{2+} ions adsorption on HA is mixed. It involves the ability of HA immobilize various metal ions due to ion exchange, and formation of insoluble phases of metal phosphates on the surface of sorbent.

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СОРБЦІЙНІ ВЛАСТИВОСТІ КОМПОЗИТНИХ МАТЕРІАЛІВ НА ОСНОВІ ГІДРОКСИАПАТИТУ В АЛЬГІНАТНІЙ ОБОЛОНЦІ

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Резюме. *Композитні матеріали на основі гідроксиапатиту широко використовуються для лікування кісткових дефектів завдяки їх біосумісності та остеопровідності. В даній роботі його було вдало поєднано з альгінатом – біополімером з гелеутворюючою здатністю. Порівняні сорбційні властивості отриманих композитних матеріалів до йонів* Cu^{2+} *та* Zn^{2+}*. Показано, що сорбція йонів* Zn^{2+} *є більш ефективною завдяки особливостям даного йону та формуванню нової нерозчинної фази при контакті з поверхнею капсул.*

Ключові слова: *гідроксиапатит, сорбція, альгінат, композит.*