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Enzymatic hydroxyapatite as a carrier for yttrium-90 and copper and ruthenium radionuclides

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S1. HAP_E. Calcium phosphates synthesized by enzymatic hydrolysis of calcium glycerophosphate in the presence of the enzyme alkaline phosphatase. The hydrolysis reaction of glycerophosphate started by adding an enzyme solution to a solution of calcium glycerophosphate. The working concentration of the enzyme in the reaction mixture was 30 mg dm^{-3}. In the process of hydrolysis, phosphate ion began to enter to the solution, and an insoluble calcium phosphate precipitate formed. The reaction time varied from 8 hours to 7 days. The resulting solid phase characterized by X-ray phase analysis.

S2.

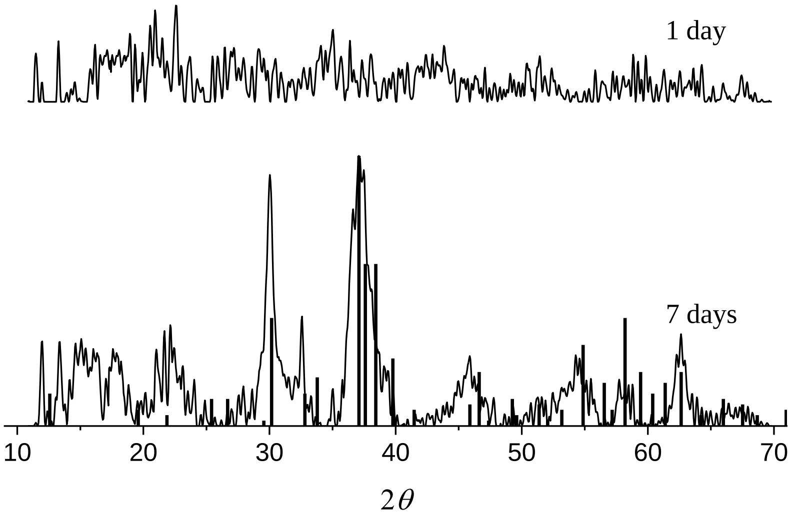

Figure S2. X-Ray phase analysis data for samples synthesized by enzymatic hydrolysis of calcium glycerophosphate in the presence of the alkaline phosphatase in 1 day (top graph) and 7 days (bottom graph) after the reaction start. HAP standard data (#09-0422) are shown with vertical bars

S3. Calcium phosphates synthesized by enzymatic hydrolysis of calcium glycerophosphate in the presence of the enzyme alkaline phosphatase. The hydrolysis reaction of glycerophosphate started by adding an enzyme solution to a solution of calcium glycerophosphate. The working concentration of the enzyme in the reaction mixture was 30 mg dm^{-3}. In the process of hydrolysis, phosphate ion began to enter to the solution, and an insoluble calcium phosphate precipitate formed. The reaction time varied from 8 hours to 7 days**.**

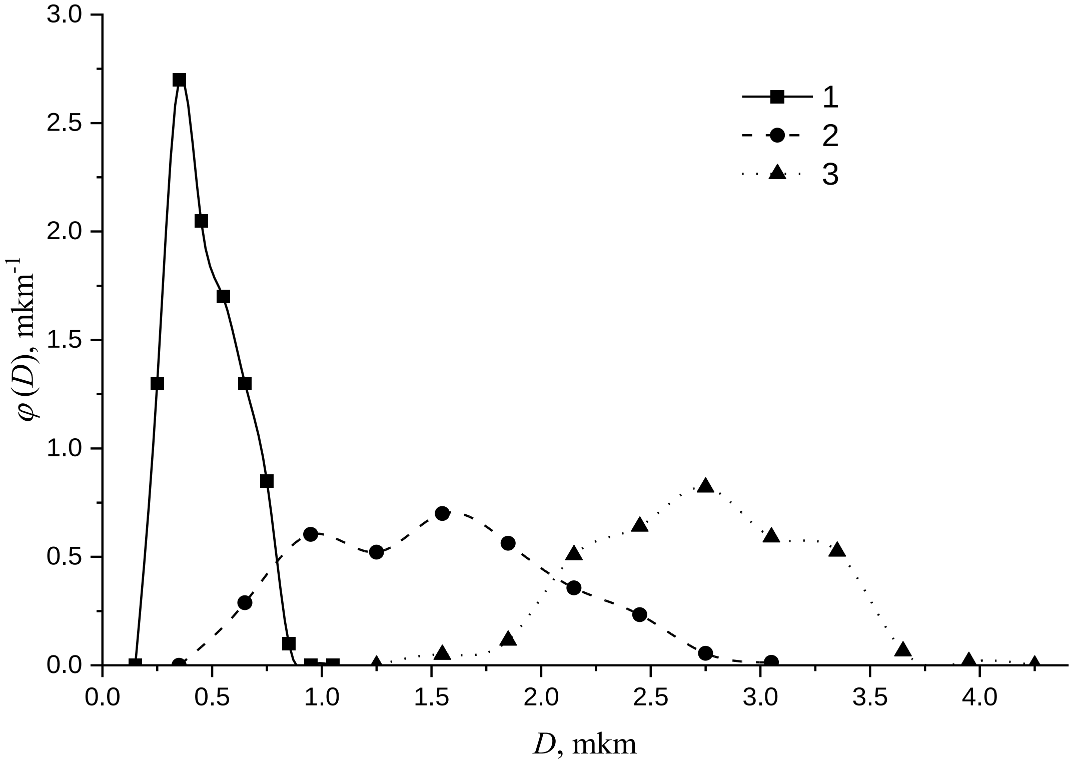

Figure S3. Differential distribution functions of particle diameter for samples synthesized by enzymatic hydrolysis of calcium glycerophosphate in the presence of the alkaline phosphatase in 1 hour (1), 1 day (2), and 7 days (3) after the start of the reaction.

S4. Measurement of specific surface area by nitrogen adsorption. Low-temperature nitrogen adsorption-desorption isotherms were obtained on an ASAP2000 automatic porometer (Micromeritics, United States). Before measurements, all samples evacuated at a temperature of 60° C and a pressure of 10^{-3} mm Hg. within 12 hours. The BET specific surface area calculated at 77 K using the Micromeritics software package. The volume of micropores determined by the t-plot method. The pore volume, including adsorption in micropores, mesopores, and on the outer surface, calculated from the amount of adsorbed nitrogen at a relative pressure $p/p0 = 0.95$.

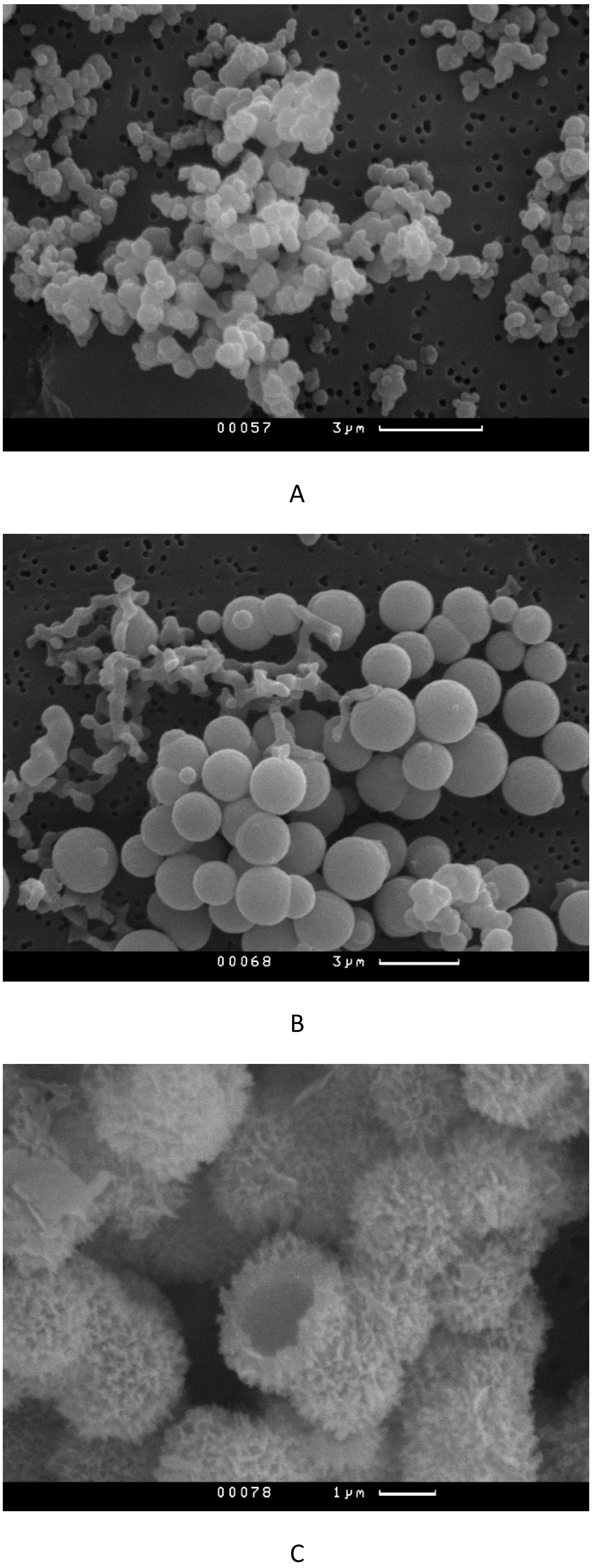

Figure S5. Scanning electron microscopy data of HAP_E samples synthesized by enzymatic hydrolysis of calcium glycerophosphate in the presence of the alkaline phosphatase in 1 hour (a), 1 day (b), and 7 days (c) after the reaction start.

S6. Sorption and desorption of yttrium-90 was carried out with an yttrium nitrate solution as a carrier. Sorption. The tubes filled with 15 mg of dry HAP_E, 0.9 ml of water, 1 ml of $Y(NO_3)_3$ solution (C = 75 g dm^{-3}) and added 100 µl of $^{90}Y(NO_3)_3$ solution . The contents mixed by a Multi Bio RS-24 rotator (BioSan, Latvia) for 0.25; 0.5;1; 2; 3; 48; 168 h. The precipitate separated and the count rate of yttrium-90 measured by Cherenkov radiation on a TRI-CARB 1500 TR (PerkinElmer, USA) liquid scintillation spectrometer. Desorption. 1 ml of saline or 1 mL BSA (C = 48 g dm^{-1}) or 1 ml acetate buffer (pH 5) added to 1 ml of solution obtained in the case of sorption with t = 1 h. The contents stirred for 2 h, 1, 5, 7 days. The yttrium yield determined by the counting rate ^{90}Y. Sorption isotherm. 15 mg of dry HAP_E, 0.9 ml $Y(NO_3)_3$ solution (C = 300; 150; 60; 6; 3 g dm^{-3}) and 100 µl $^{90}Y(NO_3)_3$ solution stirred for a week. The precipitates separated and the ^{90}Y count rate measured in the centrifugate.

S7. Copper in solutions determined by spectrophotometry in the form of an ammonia complex (Shimadzu UV-1280, λ = 620 nm). Sorption. The tubes filled with 15 mg of dry HAP_E, 1 ml of $CuCl_2$ $2H_2O$ (C = 2.152 mg ml^{-1} for copper) stirred for 1; 5; 10; 15; 30; 45 min and 1; 4; 10; 24 h. The precipitate was separated and copper determined. Sorption isotherm. 15 mg dry HAP_E, 0.1-1 ml $CuCl_2$ (C = 4.544 g l^{-1}) and H2O added up to 1 ml were stirred for 24 h. The precipitate was separated and copper was determined in the centrifugate.

S8. Ruthenium-103 ($T_{1/2}$ = 39.8 days, beta decay) obtained at INR RAS. Thorium foil irradiated by protons from 120 to 90 MeV. The irradiated foil was dissolved in 7 M HNO_3 with HF addition. Thorium separated by extraction with D2EHPA. Ruthenium was isolated from the aqueous phase on the DGA resin. ^{103}Ru is obtained in a nitric acid medium, but in order to avoid complete dissolution of hydroxyapatite, this solution brought with 10% ammonia solution to pH = 5. The radioactivity measured by a GC 3020 Canberra gamma spectrometer (USA) (gamma-line 497 keV). Sorption (carrier-free). 15 mg of HAP_E, 1.5 ml of H_2O, 600 μl of 10% ammonia solution and 100 μl of $^{103}RuCl_3$ solution stirred for 15; 60; 180; 1440 minutes The precipitate is separated and ^{103}Ru measured on a gamma spectrometer. Sorption (with a carrier). 15 mg HAP_E, 1.05 ml H_2O, 0.5 mL $RuCl_3$ (C = 5 g dm^{-3}), 100 μl $^{103}RuCl_3$ and 10% ammonia solutions (to pH 3.0) stirred for 0.25; 1; 3; 24 h. The precipitate separated and ^{103}Ru determined by a gamma spectrometer.