Ultrasonic Assisted Synthesis of Hydroxyapatite

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1. Introduction

Hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ (HAP) is the material closest to the bone tissue in its chemical and crystallographic composition [1]. It is widely used nowadays as a substituting material in dentistry, for bone traumas and as an important component in various composite materials destined for medical applications, since it has such characteristics as biocompatibility, osteoconductivity and bioactivity [2]. A wide spectrum of HAP use defines the variety of requirements for the size of its crystals, their morphology, adsorption properties, ability to aggregate, speed of their dissolution, etc. The aim of this work is to study the effect of ultrasound parameters on the structure, size and morphology of hydroxyapatite particles.

2. Materials and Methods

Hydroxyapatite synthesis (HAP) was carried out through the chemical reaction of CaO with phosphoric acid (H_3PO_4) in aqueous medium:

$$10CaO + 6H_3PO_4 = Ca_{10}(PO_4)_6(OH)_2 + 8H_2O.$$

The results are evaluated by X-ray diffraction, Transmission Electron Microscopy, morphological and sedimentation analyses.

The reactor employed for hydroxyapatite synthesis was a cylindrical Teflon vessel, 50 mm in diameter and 100 mm in height. 0.88 MHz and 2.64 MHz replaceable piezoceramic radiators were mounted on the sidewall of the vessel. The 22 kHz sonotrode radiator was brought into the vessel through the central opening in the reactor head. The radiator could be moved vertically. Phosphoric acid inlet was a ceramic pipe of 1 mm in diameter, which was put through the reactor sidewall and was oriented perpendicularly to the surface of high-frequency ultrasound radiator. The pipe could be moved in the horizontal plane. The acid feed rate in each case was 0.01 ml/s.

While the frequency and intensity of ultrasound were varied (ref. Table 1), the acoustic power was estimated with the thermal method [3]. Relative cavitation intensity of various ultrasonic regimes was evaluated according to the speed of KI oxidation [4] in hydrodynamic conditions of the HAP synthesis. Cavitometer IC-3MS (BSUIR, Minsk, Belarus) with the needle-like hydrophone of 3 mm in diameter was used for monitoring the cavitation activity during the HAP synthesis.

3. Results

All the peaks in the XRD pattern of synthesized samples are attributed to stoichiometric HAP and no other calcium phosphate peaks were detected. A high consistency between

the data was observed with JCPDS No. 09-0432.

Observation of the behavior of suspensions during their sedimentation also showed that the sample US (1.76 MHz) was significantly different from all the other samples – fine suspension remained stable for three weeks after synthesis and was partially preserved after centrifugation at 6000g, while for the remaining samples the characteristic sedimentation time was 1–3 days.

Table 1. Experimental conditions of hydroxyapatite synthesis and average length and width of hydroxyapatite particles obtained from the TEM data.

Synthesis conditions	Acoustic intensity (W/cm^2)	$L_{av.}$ (nm)	$W_{av.}$ (nm)
Without ultrasound	-	115	30
US (22 kHz)	25	91	20
US (22 kHz)*	25	45	12
US (0.88 MHz)	2.7	97	20
US (2.64 MHz)	0.2	97	27
US (1.76 MHz)	1.7	27	4

* The source of ultrasound (radiator) was located 5 mm away from the acid inlet

Table 1 shows the average values of the length and width of hydroxyapatite particles ($L_{av.}$ and $W_{av.}$). It is obvious from the data in Table 1 that variations of the ultrasound frequency and intensity in the process of hydroxyapatite synthesis lead to a decrease in the crystal sizes both for low and high frequencies if cavitation is generated. It should be noted that this decrease was weakly dependent on the cavitation intensity. The exception was the sample US (22 kHz) when radiating surface was put at 5 mm from the point of the acid inlet.

The explanation of observed results is based on the idea of formation of vortices at the interface between phosphoric acid and calcium hydroxide solution where the nucleation of hydroxyapatite particles is taken place. Smaller vortices formed at high frequency non-cavitation ultrasound regime provide smaller nucleation sites and smaller resulting particles, compared to vortices and particles obtained without ultrasound.

4. Conclusion

The formation of hydroxyapatite nanocrystals occurs at the place of mixing of calcium hydroxide and phosphoric acid. The interaction between sound waves in the reactor, containing solution of calcium hydroxide, and the jet of phosphoric acid pumped into the reaction mixture, creates vortices at the interface between reagents. Low intensity, high frequency ultrasound in the absence of cavitation, creates smaller vortices compared to the process without ultrasound. As a consequence, the smaller size of nanoparticles formed at the interface of the reagents in the presence of acoustic waves. The discovered method of synthesis has a potential to control nanoparticles size by acoustic or hydrodynamic means.

References

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