Deniz Kestanesi Kabuğundan Nano Boyutlu Whitlockite Biyoseramik Ön Malzemesinin Sentezi

Synthesis of Nano Size Whitlockite Bioceramic Precursor from Sea Urchin Skeleton

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***Özetçe*—Bu çalışmada nano boyutta biyoseramikte üretiminde kullanılabilecek olan whitlockitın, deniz kestanesi kabuğundan üretilmiş olan CaO kullanılarak modifiye edilmiş kimyasal çöktürme yöntemi ile 800 °C de 2 saat kalsine edilerek sentezlenme yöntemi tanımlanmıştır. Deniz kestanesi kabuğunun ve deneysel olarak elde edilen bileşiklerin faz bileşimleri, morfoloji ve ortalama parçacık boyutları sırasıyla X-Işını Difraksiyonu (XRD), Kızılötesi (FTIR), Differensiyel Termal Analiz (DTA) ve Elektron mikroskobu (SEM) kullanılarak belirlenmiştir. Karakterizasyon çalışmaları nano boyutlu whitlockitın (trikalsiyum fosfat) çökeltme yardımcı katı hal yöntemiyle ortalama 100 nm boyutta homojen bir yapıda üretilebileceğini göstermiştir. Sonuç olarak biyomedikal uygulamalarda kullanılmak üzere nano boyutta trikalsiyum fosfatın deniz canlılarından olan deniz kestanesi kabuğundan basit ve etkili bir şekilde üretilebileceğini belirlenmiştir.**

***Anahtar Kelimeler* — Whitlockite, Tricalcium phosphate, Biyoseramik, Deniz Kestanesi Kabuğu.**

***Abstract*— The present study describes a synthesis of nano size whitlockite bioceramic precursor using CaO obtained from sea urchin skeleton by modified wet-chemical precipitation route at 800 °C for 2 hrs. Phase composition, morphology and average particle size of sea urchin skeleton and the obtained compounds were identified and characterized by X-ray diffraction (XRD), Fourier transform infrared (FTIR) analyses, differential thermal analyses (DTA) and scanning electron microscopy (SEM). The characterization studies indicated that nano size whitlockite (tricalcium phosphate) could be produced as the homogenous phase with nano size of about 100 nm by the precipitation assisted solid state method. It means that whitlockite as nano size precursor can be easily synthesized from marine specie 'sea urchin skeleton' by a simple and efficient method for biomedical applications.**

Keywords —Whitlockite, Tricalcium phosphate, Bioceramic, Sea urchin skeleton.

I. INTRODUCTION

Whitlockite has nearly similar crystal structure with tricalcium phosphate but it contains a little amount of magnesium so it is different from tricalcium phosphate [1]. It may be used as grafts for bone repair applications [2], bone fillers and artificial tooth roots like tricalcium phosphate that can bound directly with hard tissues without fibrous connective tissues [3]. Whitlockite can be synthesized from calcium sources which are analytical grade chemical compounds or biogenic materials like eggshells[4], seashells [2] and corals [5].

In the present study, the skeleton of sea urchin was used to obtain nano size whitlockite as calcium phosphates-based bioceramic precursor. Sea urchins have spherical body structures completely covered by many sharp spines and nearly half of their body weights consist of the skeleton, usually called theca or test, which contains nearly 90 % minerals and 5 % proteins [6]. Some parts of the world, sea urchins are consumed as a food and commercially harvested and for this facilities, sea urchin skeleton may become major waste [7].

II. MATERIALS AND METHODS

Sea urchin skeleton were collected at Foca in Izmir, Turkiye and after drying process, the skeletons were ground by planetary ball mill (PC 200). As-obtained powders were calcined at 1050 °C for 2 hours to obtain CaO. The calcination temperature was selected depending on the DTA and TG results (figures not given in text). The experimental method for production of calcium phosphate, whitlockite, was based on the investigation conducted by Salma et al. [8] with some modification. H_3PO_4 solution (0.5 M) was slowly added with drop wise method (~0.75 ml/min under vigorous stirring) to the calcium oxide suspension until the stabilizing ending pH at 6. The suspension was kept at 80° for 4 hours with continuously stirring. After that, the suspension was filtrated and gel form was dried at 105°C for overnight and ground in a mortar. The obtained powder was sintered 800 °C for 2 hours.

The phase compositions and crystallinity of the samples were identified by X-ray powder diffraction (XRD) using Rigaku Miniflex 600 Diffractometer with Cu Kα (40 kV, 15 mA, k = 1.54050 Å) radiation. The thermal behavior of products as well as their chemical stability and the morphology and average particle size of the synthesized bioceramic precursor were determined Setaram Labsys TGA/DTA simultaneous thermogravimetric analyzer and differential thermal analyzer and LeO EVO 40 scanning electron microscope, respectively.

III. RESULT AND DISCUSSION

Figure 1 shows the XRD pattern of the raw sea urchin skeleton, CaO (obtained from sea urchin skeleton) and the synthesis whitlockite. An analysis of the powder XRD data of sea urchin skeleton proved that actually most intense reflections could be assigned to the calcium carbonate with a little amount of magnesium carbonate (nearly 2 % of all structure). In the present study, the structure of sea urchin skeleton was defined as magnesium calcium carbonate with ($Mg_{0.06}Ca_{0.94})(CO_3)$ chemical formula since the all patterns match well with the powder diffraction data reported in JCPDS Card No: 01-089-1306. After calcination of the sea urchin skeleton, it was seen from the Figure 1 that, synthesized powder composed of CaO predominantly. Nearly all peaks belonged to CaO was found to being a good aggrement with those reported in JCPDS file 48-1467. The XRD pattern of the tricalcium phosphate indicated that the obtained material was a whitlockite which is a rare phosphate mineral and magnesium is partly substituted for calcium [9]. The source of the magnesium is the skeleton and the solubility of skeletal is partly prevented by the incorporation of magnesium ions [6] and on the other hand, it is very useful to promote bone cell adhesion, differentiation and proliferation [10].

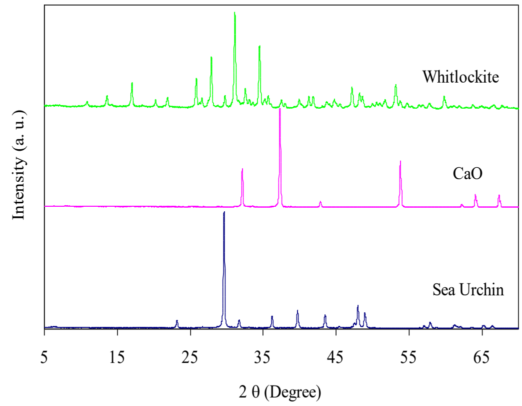

Figure 1. Powder X-ray diffraction patterns of the sea urchin skeleton, CaO and whitlockite.

The photo of the sea urchin skeleton is represented in Figure 2 (a) and in the same figure SEM micrographs for the sea urchin skeleton, CaO and the whitlockite are depicted. It can be seen that the sea urchin skeleton (b) consisted of crystal-like structures of non-uniform morphology and the calcinated sea urchin skeleton (CaO in Figure 2. c) indicates irregular particle shapes with agglomeration structure demonstrating high temperature calcination procedure. Figure 2.d indicates that the synthesis route has shown significant effect on particle size and morphology. The whitlockite can be synthesized as nano size with uniform size distrubition which is very important for biomedical applications.

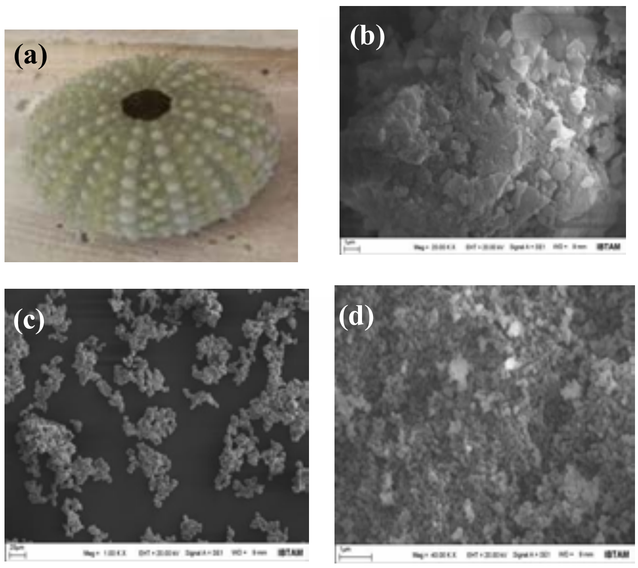

Figure 2. The photo of sea urchin skeleton (a) and SEM images of sea urchin skeleton (b), CaO (c) and whitlockite bioceremic precursor (d)

IV. CONCLUSION

In the present study, nano size whitlockite bioceramic based precursor was successfully synthesized using CaO, calcinated from the sea urchin skeleton, by simple modified wet precipitation method. In the literature, it was the first time, the sea urchin skeleton was used as a starting material to obtained calcium based ceramic precursors. This selection would be helpful not only to contributes the waste assessment, but also to create an effective and cheap material. In addition, it is suggested that the sea urchin skeleton should be collected from the commercially harvested facilities or non-polluted sea waters.

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KAYNAKÇA

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