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# The Optimization of the Hydroxyapatite (HA) Material Characteristics Produced From Corbiculacea (Etok) Shells

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**Abstract.** Hydroxyapatite commonly used in medical field for tissue disease, bone disease, drug delivery and also for non-medical field purpose such as wastewater treatment. Due to excellent biocompatibility and bioactive properties, hydroxyapatite (HA) which is a group of calcium phosphate (CaP) and similar to the natural bone composition has been broadly ventured in medical area. Synthesizing the HA was done via precipitation method by implementing the *Corbiculacea* (Etok) shells as the resource of calcium precursors. Calcination of *Corbiculacea* (Etok) shells took place to convert calcium carbonate ( $CaCO_3$ ) to calcium oxide ( $CaO$ ).  $CaO$  were then reacted with water to form calcium hydroxide ( $Ca(OH)_2$ ) and later, reacted with phosphoric acid ( $H_3PO_4$ ). This experiment manipulated the CaP ratio to study the properties HA formed. CaP ratios used are 1.50, 1.67 and 2.00. The characterization were performed using Energy Dispersive X-Ray Spectroscopy (EDS), Scanning Electron Microscopy (SEM) and Fourier Transformation Infrared (FTIR).

## 1. Introduction

Bone tissue defects due to injury are a major concern in orthopedic surgery [1]. Technology on biomaterials product had produced autologous bone grafts and allografts to overcome the defect extensively in orthopedic field. The chemical formula of hydroxyapatite (HA) is  $(Ca_{10}(PO_4)_6(OH)_2)$  and it is widely used in orthopedic and biomedical application [1]. HA's chemical composition is similar to the natural bone, thus encourage the production of synthetic bone which is predominantly based on HA material [2-5]. HA can be synthesized using various methods and the most practical method is by the precipitation method. In this study, precipitation was chosen due to its simplicity and convenience. Recently, the interest of utilizing waste materials for various applications had increased. Hence, the potential biomaterials product from the shell wastes especially due to the high content of  $CaCO_3$  could be further ventured [6]. To date, the study of HA based on Malaysian seashells apart from common cockle (*Anadara Granosa*) can be further explored. Therefore, the objective of this study is to determine the characteristics of HA from *Corbiculacea* (Etok) shell and manipulating Ca/P ratio in synthesizing HA.



## 2. Material and methods

### 2.1 Materials

Corbiculacea (Etok) shells were purchased from local market in Kelantan. Phosphoric acid with 95% and ammonia with 25% were purchased from Merck. The chemical is used without further purification.

### 2.2 Synthesis of Hydroxyapatite

*Corbiculacea* (Etok) shells were cleaned from debris before further process. Ammonia and phosphoric acid were purchased from Merck and directly used without any purification. The first step was to crush and sieve the shells into micrometre size to fasten the process of calcination. High temperature was used for calcination which is about 1000°C in 90 minutes to produce calcium oxide (CaO). CaO was then reacted with distilled water to produced calcium hydroxide ( $Ca(OH)_2$ ). This was followed by the addition of phosphoric acid ( $H_3PO_4$ ) via titration. The phosphoric acid as supplied was added in different amounts; 1.80ml, 1.64 ml and 1.35ml in respective to the 1.50, 1.67 and 2.00 Ca/P ratio. While titration of phosphoric acid ( $H_3PO_4$ ) took place, the ammonium solution was added drop wise at rate 5.5ml/minutes to maintain the solution at pH 11. The solution was let to age over night to produce HA precipitation. After 24 hours, the solution was filtered and the precipitation was washed with distilled water followed by drying. After that, the dried HA was powdered by using mortar and pestle.

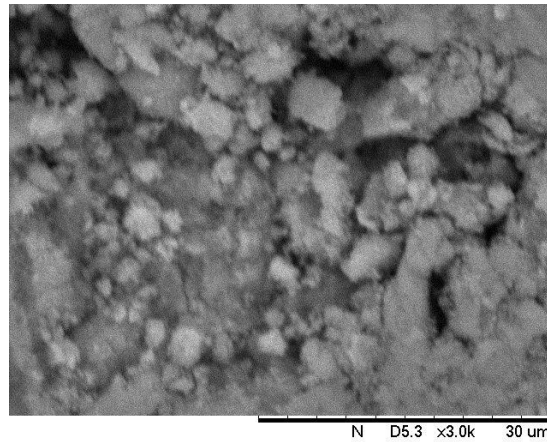
### 2.3 Characterization of Hydroxyapatite powder

There are few test performed for the characterization of HA nanocrystals made from *Corbiculacea* (Etok) shells. The first test was Scanning Electron Microscopy (SEM) to study the morphology of the HA via HITACHI TM 3000 Tabletop Microscope. The same testing modality was used for Energy Dispersive X-ray Spectrometry (EDS) which determine the chemical elements existed in the synthesized HA. The third test was Fourier transform infrared spectroscopy (FTIR) for determining the functional group of a pure HA using Perkin Elmer Spectrum 65 through KBr method. EDS was carried out to determine the element or chemical composition of the hydroxyapatite. Three varieties Ca/P ratio used in this study which is 1.50, 1.67 and 2.00. Three variety of parameter used in this studies showed that compositional analysis of powders reveals the presence of Ca, P and O elements. The larger peaks for hydroxyapatite were O elements and comparatively smaller peaks for Ca and P elements.

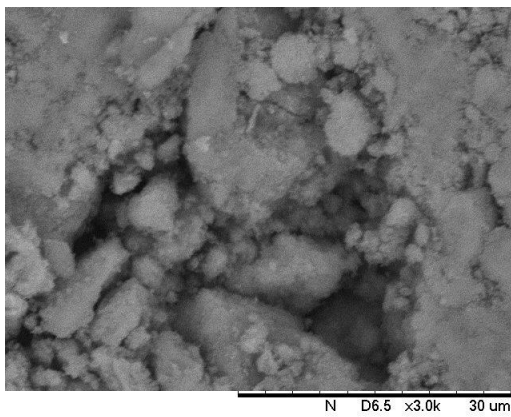
## 3. Result and Discussion

### 3.1 Scanning Electron Microscopy (SEM)

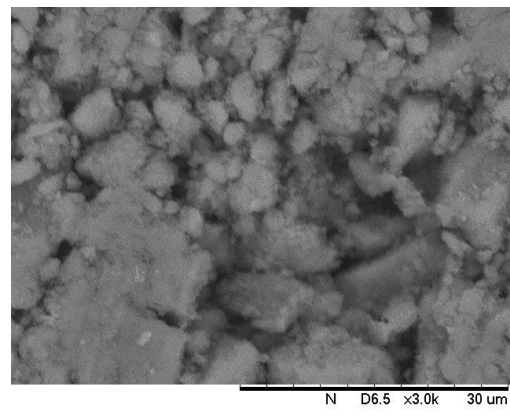
The purpose of SEM is to determine the morphology of the HA powdered. Figure 1, 2 and 3 shows the image of HA morphology with different Ca/P ratio. The morphology of the HA images are shown below with different Ca/P molar ratio. HA with Ca/P ratio 1.67 shows less agglomeration meanwhile for HA with Ca/P ratio 1.50 and 2.00 show a more agglomerated HA powder. Agglomeration occurs due to the van der Waals attraction between HAP during calcination process [7]. All samples show uniform and spherical shape, although irregular. Basically, the temperature used during calcination process will affect the morphology of the particles [6]. Another factor that will affect the morphology of the HA is the phosphate-containing solutions. This had consequently affected the morphology of the HA obtained, for example platelet-like, needle like, or rod-like microstructure [8]. Thus, the morphology of HA can be optimized by the phosphate solution.



**Figure 2.** SEM image for Ca/P 1.67



**Figure 1.** SEM image for Ca/P 1.50



**Figure 3.** SEM image for Ca/P 2.00

### 3.2 Energy Dispersive X-ray Spectrometry (EDS)

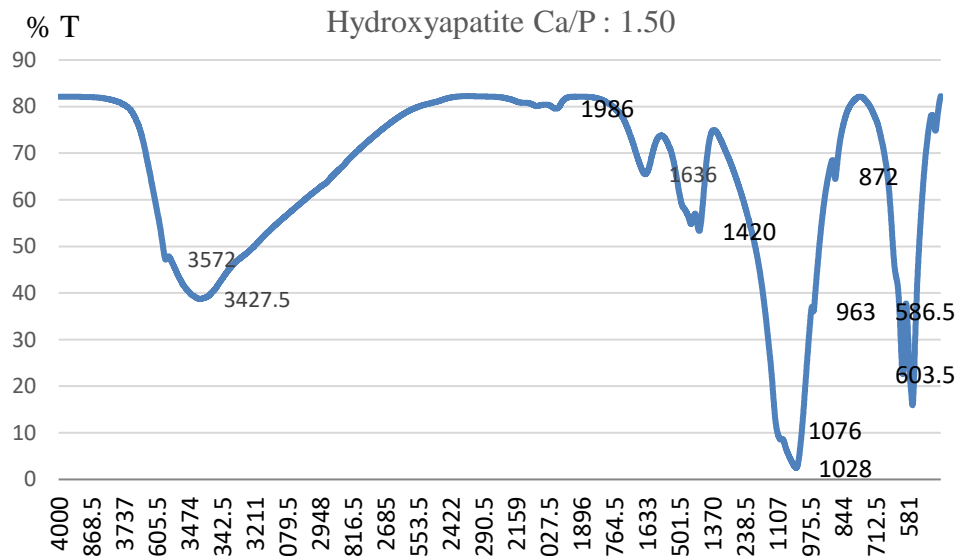
Three varieties of Ca/P ratio was used in this study which is 1.50, 1.67 and 2.00. The result EDS analysis from Table 1 showed that the actual result HA Ca/P ratio is different from calculation as much as  $0.03\pm$  to  $0.08\pm$ . Besides, EDS showed that compositional powders consist of Calcium (Ca), Phosphorus (P) and Oxygen (O) elements. The larger peaks for HA is an O element and comparatively smaller peaks for Ca and P elements. Increasing the Ca/P ratio showed an increment of O element which might contribute from oxide mass during calcination.

**Table 1.** Result of EDS

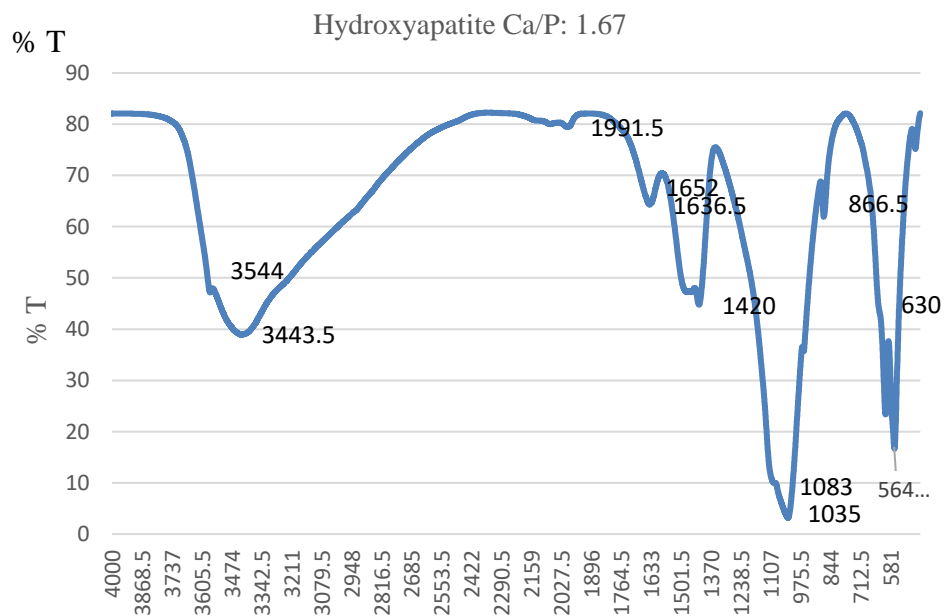
HA Ca/P molar ratio	Element O Atomic %	Element Ca Atomic %	Element P Atomic %	Result HA Ca/P ratio
1.50	72.21	17.04	10.76	1.58
1.67	73.07	16.73	10.20	1.64
2.00	77.15	15.38	7.48	2.05

### 3.3 Fourier Transform Infrared Spectroscopy (FTIR)

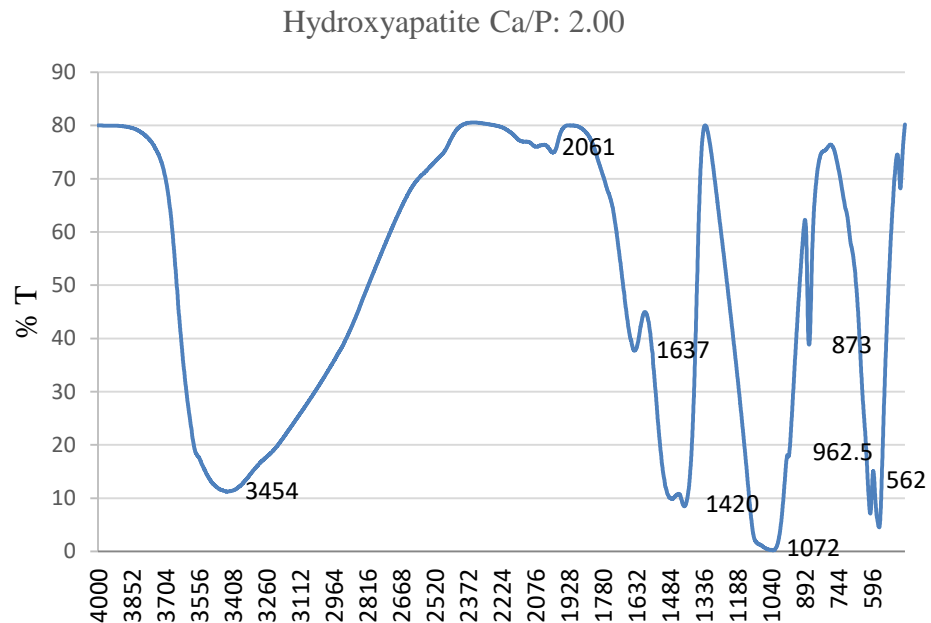
FT-IR wave spectrum presented in Figure 4.0, 5.0 and 6.0 for Ca/P ratio 1.50, 1.67 and 2.0 respectively. There were eight clear peaks exist in the spectrum for both HA sample pH 6 and pH 12. Whereas, there were nine distinct peaks in HA sample pH 7. Phosphate, hydroxyl and carbonate bond/group were present among those peaks.



**Figure 4.** HA spectra with Ca/P ratio 1.50



**Figure 5.** HA spectra with Ca/P ratio 1.67



**Figure 6.** HA spectra with Ca/P ratio 2.00

Figure 4 above showed the FTIR spectrum for hydroxyapatite with Ca/P 1.50. At bands  $3572\text{cm}^{-1}$ , stretching vibration of free hydroxyl group happened. Phosphate group absorption in HA at range  $1028\text{cm}^{-1}$  to  $1076\text{cm}^{-1}$ . The  $\text{PO}_4^{-3}$  v<sub>4</sub> mode can be found at  $586.5\text{cm}^{-1}$  and  $603.5\text{cm}^{-1}$ . The band at  $872\text{cm}^{-1}$  indicates the presence of  $\text{CO}_3^{-2}$  group appeared [8]. Meanwhile, Figure 5 shows the FTIR spectra of HA with Ca/P 1.67. Band at  $1636.5\text{cm}^{-1}$  corresponds to the stretching mode of HO- and stretching vibration of phosphate group took place at  $1083\text{cm}^{-1}$  and  $1035\text{cm}^{-1}$ . Band at  $564.5\text{cm}^{-1}$  corresponds to  $\text{PO}_4^{-3}$  which is present at calcined sample [9]. The peak of band at  $3443.5\text{cm}^{-1}$  is a typical assignment of stretching mode  $\text{OH}^-$  ion [10]. A context of pure HA structure should not present any elements of carbonate vibration mode at  $1420\text{cm}^{-1}$ . The presence may due to atmospheric adsorption after the synthesis process which is unavoidable in chemical synthesis technique [10]. Last is Figure 6; HA with Ca/P molar ratio 2.00. The phosphate ions,  $\text{PO}_4^{-3}$  are a principal molecular component in HA given in IR absorbance in range of  $550\text{cm}^{-1}$  to  $1200\text{cm}^{-1}$  regions. At bands  $873\text{cm}^{-1}$  and  $1080\text{cm}^{-1}$  correspond to the stretching vibration of  $\text{PO}_4^{-3}$  and  $562\text{cm}^{-1}$  due to bending of  $\text{PO}_4^{-3}$ . Stretching mode of  $\text{OH}^-$  ions occurs at peak  $3453\text{cm}^{-1}$ . One of the distinct bands was observed at  $1637\text{cm}^{-1}$  which rise from stretching mode and bending mode molecules of  $\text{OH}^-$  [11].

#### 4. Conclusion

In conclusion, HA can be synthesized from Corbiculacea (Etok) shells and the Ca/P ratio affects the HA characteristic. It was clear that each of the samples exhibited distinct features proved by the SEM and the EDS analysis. All HA made with Corbiculacea (Etok) shells exhibited three main chemical compositions present in the commercialized HA such as Calcium, Phosphorous and Oxygen. As for FTIR analysis, the presence of  $\text{HPO}_4^{2-}$  and  $\text{OH}^-$  groups in all three samples confirmed the formation of HA. The presences of  $\text{CO}_3^{2-}$  band in all samples were because of the air contamination after the calcination of Corbiculacea (Etok) shells and during HA synthesizing process.

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