Hydrothermal Synthesis of Hydroxyapatite From Cockle Shell Waste

Yelmida Azis,[a,*] Zultiniar,[a] Novesar Jamarun,[b] Syukri Arief,[b] and Hadi Nur,[c]

[a)]*Chemical Engineering Department, Riau University, Indonesia*[1)]
[b)]*The Faculty of Mathematics and Science, Andalas University, Indonesia*[2)]
[c)]*The Ibnu Sina Institute for Fundamental Science Studies, Universiti Teknologi Malaysia*[3)]

*Corresponding author: yelmida_azis@yahoo.com

Paper History

Received: 12-October-2014
Accepted: 13-November-2014

ABSTRACT

The hydroxyapatite synthesis of cockle shell (*Anadara granosa*) as a source of calcium was done by using hydrothermal method. Hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$(HAp) is widely used in medical fields especially as a bone and teeth substitute. First step, the cockle shell were calcined at 900◦C for5 hours. The CaO of cockle shell was converted to Precipitated Calcium Carbonated (PCC) by using the carbonation method. The hydrothermal process of PCC was done at 140^{O}C for 16 hours and hydroxyapatite obtained.The forming of biomaterial hydroxyapatite was characterized based on XRD, FTIR, SEM-EDX. The XRD patternsshowed that the products were crystallized hydroxyapatite. The morphology of hydroxyapatite viewed under SEM showed that uniformly crystals of hydroxyapatite.

KEYWORDS*: cockle shell, hydroxyapatite, hydrothermal, Precipitated Calcium Carbonated*

1.0. INTRODUCTION

Indonesia is very rich with the sources of calcium, both from natural sources (egg shells, corals, cockle shells, bones) and in the form of natural product (limestone) [1]. Kerang darah shells (*Anadara granosa*) is one of the potential calcium sources, a lenient animal (mollusca) of bivalvia class. Moreover, 95% main composition of kerang darah shells is in the form of $CaCO_3$ [2]. Kerang darah shells' calcium could be processed into the products that are more efficient in the industry or medical world, like Precipitated Calcium Carbonated (PCC) and hydroxyapatite (HAp).

PCC is a calcium carbonate compound ($CaCO_3$) that can be processed from the shells material through a series of chemical reactions. PCC particles' is homogeneous that in the same size with micro-scale particle [3]. Currently, PCC widely used in industrial project as an addictive of pharmaceuticals, food, paper, plastic and ink. Previously, PCC has been used as a base material in the synthesis of carbonate apatite. Its high level's purity as well as the small size and constancy of the particles, turn out to be PCC advantage to be changed into apatite compounds [4].

The hydroxyapatite has been broadly used in the biomedical field for filler and coating of bone and dental implants [5,6]. Besides, because of its spongy structure that possess chemical and thermal resistance, the hydroxyapatite has also been widely used as a catalyst or adsorbent [7, 8, 9]. Furthermore, the PCC in this study is made of cockle shells through carbonation method, which will be processed with further method of hydrotermal and synthesized into hydroxyapatite. Based on morphological pattern, particle size and the purity of the Hap powder results, affect the properties of Hap that will be applied in the orthopedics fields, dental materials, as well as for catalyst or adsorbent. It is hoped that through the hydrothermal process, the PCC that made from precursor shellswaste, will be formed HAp that have smooth and identical size, so that it can be usefull in the biomedical field as a bone filler and coating for its tremendous osteoconductivity [5,6].

2.0. MATERIALS AND METHOD

The materials are the cockles shells, which is collected from Indera Giri Hulu, Riau ; diammonium hydrogen phosphate ($(NH_4)2HPO_4$) Merck ; 2M nitric acid (HNO_3) solution; ammonium hydroxide (NH_4OH) 65% Merck; CO_2 gas and aquadest. The cockle shell's samples are washed and cleaned, then dried out. After that, it will be mashed up with pulvurizer, and the powder of the cockleshells will be obtained with a smaller seize particle and will be adjusted with a sieve tray ($\pm$ 0.125 mm).

Fig.1 (a) *Kerang darah* shells and
(b) powder of *kerang darah* shells

2.1. The formation of PCC by using cockle shells (kerang darah shells)

The cockle shells' powder was calcinated in the furnace around 5 hours at 900°C, and the CaO will be obtained from that process. Then, 16,8 gram of CaO were mixed into erlenmeyer that contains of 300 mL HNO_3 2M solution. After that, the solution will be stimulated with the magnetic stirrer around 30 minutes, before it is finally filtered. In the meantime, filtrate is heated into 60°C, and added thick NH_4OH until it is reaching around pH 12 . The mixture was filtered once again, and to the filtrate the pure CO_2 gas was flowed until it is reaching pH 8 and white precipitate or known as PCC was formed. Lastly, the PCC was strained and washed several times by using distilled water. The obtained PCC then dried with ±115 °C temperature. And it will be ready to be used as the calcium source to synthesize hydroxyapatite [3].

2.2 Synthesis Hydroxyapatite of PCC

The Hydroxyapatite creation of cockle shells' PCC was made according to Hien et al procedure [10], by varying the temperature (120, 140, 160, and 180°C) and time reaction (for 14, 16, 18 and 20 hours) in the *vessel* hydrothermal.Then, 5 gram PCC was added into 15 ml saturated solution $(NH_4)_2HPO_4$ with mol ratio Ca/P = 1,67. After that, sealed vessel was placed in the oven, and the reaction process will be done in accordance to a suitable variable. The moment reaction is complete, the synthesized solids were cleanly washed by using distilled water, and will be dried out in the oven. On short, the pure dried sample was ready to be characterized.

2.3. Characterization

The characterization of hydroxyapatite will be done through *X-ray diffraction (XRD), Scanning electron microscopy (SEM)(Hitachi S-3400N), Fourier Transform Infrared Spectroscopy (FT-IR).* Not to forget the XRD and SEM analyses of PCC. The analyses of XRD is conducted in order to define the structure of PCC's crystal and the result of HAp synthesis. The SEM image is functioned to look into the morphological surface and the similarity particle of synthesis result of obtained.

3.0. RESULTS AND DISCUSSION

The synthesis of *Precipitated Calcium Carbonated (PCC)* was acquired through modified carbonation method, by adding nitric acid on the calcium oxide dissolution process. Then, the obtained PCC crystals were analyzed by using X-ray diffraction, and the results are compared with the X-ray pattern of cockle shells and standard calcium carbonate, as shown in Figure 2a. 2.b and 2c.

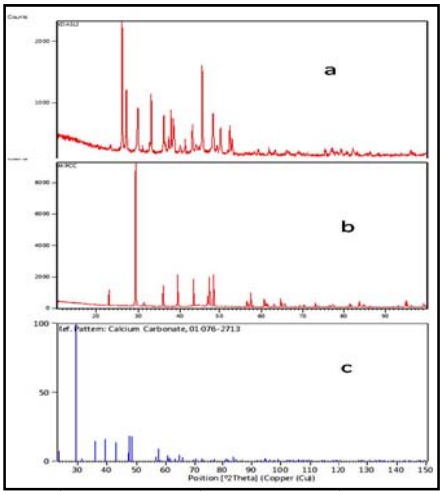

Fig. 2. Diffraction pattern of X-ray: (a) cockle shells,(b).*PCC* of cockle shells,(c).JCPDS calcium carbonate.

Diffraction patterns of X-ray *Precipitated calcium carbonated* cockle shells will be compared with the JCPDS (01-076-2713) data later. In this process, it is found three peaks with the highest intensity that match the X-ray calcium carbonate standard patterns, around the junction 2θ = 29.36; 39.37; 48.46.

SEM image of morphological PCC analyses will be figured below [with enlargement of (a) 100 and (b) 500 times]. The PCC form and size of particles that attained in the research were almost in the same size (20-30 μmeter).

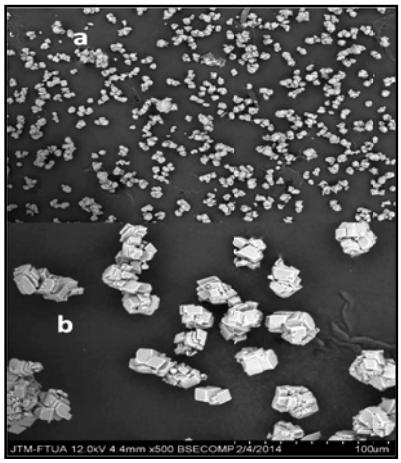

Fig. 3. SEM image of cockle shells' PCC

After that, PCC was utilized as a foundation of hydrothermal process. The temperature were varied (start from 120, 140, 160, and 180°C) and time synthesis (for 14, 16, 18 and 20 hours), as a final point, it was gained the great condition for hydroxyapatite synthesis PCC of cockle shells on 140 °C and 16 hours for the time reaction

Hien et al [10] reported the best condition of coral HAp synthesis stands in the temperature 180°Cfor 36 hours. This situation could be happen if the coral particles' size were in the large volume (5x5x5 mm) that took a long time and highest

degree of temperature to penetrate ammonium phosphate to form the apatite compound. However, this research used the very fine size of PCC particles, so that the HAp were formed at a mid-temperature.

The FTIR spectroscopy analyses to the compound of synthesis result on 140°C with time reaction nearby 16 hours, it can be seen the specific spectrum patterns for the PO_4 adsorption of hydroxyapatite (Figure 4.). Meanwhile, in the FTIR spectrum was found the P-O stretching adsorption that came from the PO_4^{3-} on 1100-950 cm^{-1}wave number, which known as the characteristics of bands for Hydroxyapatite.In addition, the asymmetric stretching (v) and bending(v4) modes of PO_4^{-3} ion were detected at around 1047.9, and 604.1 and 566.7 cm, respectively.The symmetrical stretching modes (v1 and v2) of PO_4^{-3}ion were also found at around 961.4 and470.4 cm-1, respectively[5,10].

The analyses spectroscopy result by using FTIR tools shows that there was apatite compound marked with the vibration peak of P-O and PO_4^{3-}. The fastening cluster of $PO_4^{3-}$with the Calcium could be seen with there is no NH band adsorption of ammonia or ammonium on the 3150-3500 cm^{-1}wave number.

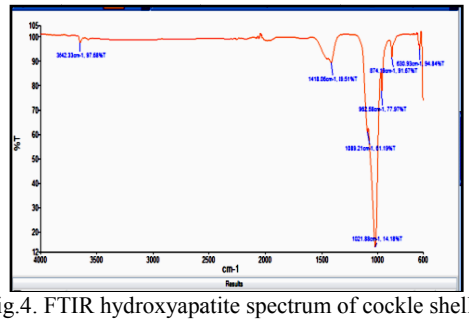

Fig.4. FTIR hydroxyapatite spectrum of cockle shells' PCC

Moreover, an analysis of X-ray diffraction to the compound of synthesis result on the temperature140°C with time reaction for 16 hours, was directed in order to analyze the obtained apatite compound. The diffractogram apatite compound patterns of synthesis result showed the similar patterns with the XRD standard of hydroxyapatite (JCPDS 01-074-9780) (Figure 5).There, it was revealed some peaks with the high intensity that suitable the X-ray hydroxyapatite standard, which are positioned on 2θ : 25,87 ; 28,87 ; 31,73 ; 32,86; 33,97 ; 39,73 ; 46,66 ; dan 49,46. Based on that analyses, it can be concluded that the synthesis result of hydroxyapatite own hexagonal crystal system.

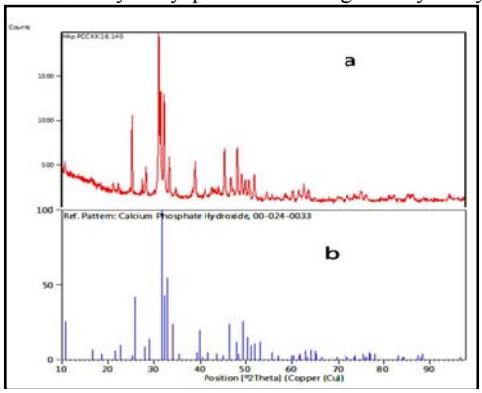

Fig.5. Diffraction patterns of X-ray(a) hydroxyapatiteof synthesis result, (b) standard of JCPDSHydroxyapatite

Figure 6 shows the SEM analysis of apatite compound of cockle shells' PCC on 140°C for 16 hours time reaction [with a. 100, b. 500, c. 1000, and d 1500 times enlargements]

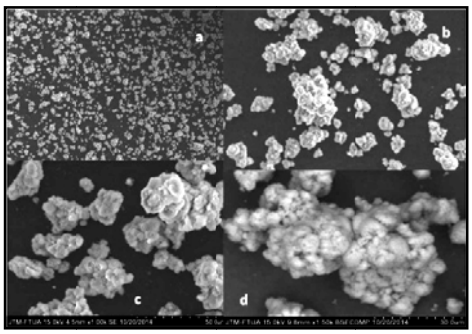

Fig.6. SEM image of hydroxyapatite compound of cockle shells' PCC

The SEM image displayed the synthesis result of hydroxyapatite compound that has the similar form and size of particles (10-50 µmeter).

4.0 CONCLUSION

The compound analysis of synthesis result, proved that the hydroxyapatite synthesis of cockle shells' waste, through the formation of Precipitated Calcium Carbonate (PCC) produced the excellent result. The shortest time of synthesis and the lower temperature degree, illustrates the advantage of the method in this research. Additionally, the tremendous synthesis HAp on140 °C for 16 hours achieved the hydroxyapatite with the Hexagonal crystal structures. As well as the X-ray diffraction patterns and characterization with FTIR are suitable compared with the standard HAp process.

ACKNOWLEDGEMENTS

The authors would like to convey a great appreciation to Dirjen Dikti for supporting this research through Dana Penelitian Desentralisasi 2014

REFERENCE

1. Kemperl,J. and Macek,J. 2009. *Precipitation of calcium carbonate from hydrated lime of variable reactivity,granulation and optical properties.* Int. J. Miner. Process. 93, pp. 84–88
2. Rashidi, N.A., Mohamed, M. and Yusup, S.2011. *World Academy of Science, Engineering and Technology 60*, pp 818-823
3. Jamarun, N., Yulfitrin, Arief,S. 2007.*Pembuatan Precipitated Kalsium karbonat (PCC) dari Batu Kapur dengan Metoda Kaustik Soda*", J.Ris.Kim.,1 (1),20-24
4. Ningsih, J.,R.2013.*Pemanfaatan Terumbu Karang Dalam Pembuatan Apatit Karbonat dan Karakterisasinya.* Thesis Program Pascasarjana Universitas Andalas , Padang
5. Ishikawa, K. (2010). *Bone Substitute Fabrication Based on Dissolution-Precipitation Reaction*. Material.**vol.** 3: 1138-

1155
6. Bingöl, O.R. and Durucan,C.2012.*Hidrotermal Synthesis of Hidroksiapatit from Calcium Sulfate Hemihydrate* ,Am. J. Biomed. Sci. , vol.4(1), 50-59
7. Garcia, B. Gonzales, G. Ocanto, F. Linares,C. F. 2012. *CoMo/Zn-hydroxyapatite as Catalysts for The Hydrodesulfurization reaction of Thiophene.* Indian Journal of Chemical Technology, vol.19, pp 403-408
8. Vazquez-Hernandez, F., Mendoza-Barrera,C, Altuzar, V. Melendez-Lira, M. Santana-Aranda, M.A.,de la,M. and Olvera,L. 2010. *Synthesis and characterization of hidroksiapatit nanoparticles and their application in protein adsorption.* Material Science and Engineering B, 174, 290-295
9. Tsuchida, T., Yoshioka, T. Sakuma, S. Takeguchi, T.,Ueda,W. 2008. *Synthesis of Biogasoline from Ethanol over Hydroxyapatite Catalyst*.Ind. Eng. Chem. Res.,47, 1443-1452
10. Hien, V.D.,.Huong, D. Q Bich,P. T.N. 2010.*Study of The Formation of Porous Hydroxyapatite Ceramics From Corals via Hydrothermal Process.*Journal of Chemistry, Vol. 48 (5), P. 591 - 596,