Application Of The Sol-Gel Hydroxhapatite Synthesis Method From Green Clam Shell

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Abstract.

Hydroxyapatite is the main mineral that makes up bones and teeth so that it has a level of similarity with the mineral parts of bones and can be used as an alternative bone substitute material. As an alternative material for bone substitution, hydroxyapatite has a fairly high economic value and is still dominated by imports from foreign countries. In an effort to reduce the level of imports of hydroxyapatite, research was carried out on green mussel shells as a source of calcium for the synthesis of hydroxyapatite. The synthesis of hydroxyapatite was carried out using the sol-gel method with raw materials for calcium precursors obtained from green mussel shells and varied concentrations of phosphoric acid (0.1 M, 0.5 M, 1 M; 1.5 M; and 2 M). Based on the analysis of the hydroxyapatite product produced using Atomic Absorption Spectrophotometry analysis, it was found that the ratio of Calcium-Phosphate (Ca/P) for H3PO4 concentrations was 0.1 M, 0.5 M, 1 M; 1.5M; and 2 M respectively by 1.73; 1.70; 1.67; 1.63; and 1.61. In addition, based on the results of the Fourier Transform Infra Red analysis, a random sample also found a Ca-O group; PO43; and OH- which is the main group of Hydroxyapatite and from SEM analysis the crystal morphology is known to be spherical, uneven and agglomerated so that in this study the synthesis of Hydroxyapatite using the sol-gel method was successfully carried out..

Keywords: *Hydroxyapatite, calcium, and sol-gel.*

I. INTRODUCTION

Indonesian waters which are quite extensive have abundant natural resources, one of which is green mussels. Green mussels are often consumed only for the meat, while the shells are not utilized optimally and are thrown away. According to the theory (Liemawan , 2015) green mussel shells have a calcium composition high carbonate that is 95.69 %. Content composition calcium high carbonate _ the can used as a source of calcium in synthesis of metal-containing compounds calcium like for example on synthesis *Hydroxyapatite* . *Hydroxyapatite* is the main mineral that makes up bones and teeth so that it has similarities with the mineral parts of bones and can be used as a bone substitute material for alternative (Mozartha , 2015) . *Hydroxyapatite* is a natural source obtained from various sources, both naturally and synthetically. *Hydroxyapatite (HAp)* . *Hydroxyapatite* is a ceramic biomaterial compound composed of calcium and phosphate with the molecular formula $Ca_{10}(PO_4)_6(OH)_2$.

Fig 1. Green Shells

Green clam *(Perna viridis)* includes soft animals *(molluscs)* that live in the sea, especially in the littoral area, have a pair of shells *(Bivalvia),* slightly bluish green in color. The gills are layered *(Lamelii branchia)* and axe-footed *(Pelecypoda)* and have *byssus threads* . Shell living green clusters and sticks

firmly by using its byssus threads *to hard* objects such as wood, bamboo, stone , or hard substrates (Cappenberg, 2008) .

Table 1. Chemical Composition on Powder shell Shell Green

No	Component	Content (% Weight)
1	$CaCO_3$	95.69
2	SiO_2	0.22
3	Fe2O3 _ _ _	1.00
4	MgO	3.08
5	Al_2O_3	0.01

Source : Liemawan , (2015)

In Indonesia there are diverse type processed food made from raw shell green . With many enthusiasts processed food made from raw shell green This so generated waste _ will the more increase . Public general often only take meat shell green just For processed whereas For the skin will go out become waste And most waste thrown away direct to environment . This is what it becomes reason main happening pollution to environment (Sunarsih , 2014). *HAp* application in the field of implantology is used to assist the bone healing process. The process of bone healing uses a substitute material or what is called *a bone graft* . *Bone graft* , which was developed as an alternative choice by researchers and surgeons, uses calcium phosphate-based materials. Meanwhile, the application of *HAp* in the field of stomatology as a bone graft material in the treatment of infrabony pockets, namely bone damage that occurs in the supporting tissues of the teeth. In several studies it was found that *HAp* synthesized using the sol-gel method was more efficient in increasing contact and interface stability between artificial bone and natural bone, both in *vitro* and *in vivo environments* . The synthesis stage in this method begins with dispersing colloidal particles in a liquid. The precursor material is mixed mechanically in a solvent with the pH adjusted to prevent precipitation. The result of this mixing will be a gel *(gelation) , a diphasic* system which consists of a solid phase *and* a liquid phase *(interstitial liquid).* The next stage is to remove the liquid phase through the drying process.

The process of forming the apatite structure of *HAp* using the sol gel method is very dependent on chemical activity and temperature in the synthesis process due to the natural chemical properties of the precursor (Yusuf, 2019) Research has been carried out by Alpina (Alpina et al . , 2017) in her research "Synthesis *of Hydroxyapatite* from *Precipitated Calcium Carbonate* (PCC) Chicken Eggshells Through *Sol - Gel Process* with Variation of pH and *Aging Time"* . In this study, the best results *of Hydroxyapatite were obtained* using the sol method . -gel with a pH of 9 and an *aging time* of 72 hours which resulted in a monoclinic crystal structure with a particle size of 53.89 nm with a Ca/P mole ratio of 1.52. As well as Oji (Oji et al , 2019) on his research " Optimization Concentration Sour Phosphate In Making *Hydroxyapatite* From waste Bone Fish Cob (*Euthinus Affinis*) with method precipitation ". On study the done synthesis *Hydroxyapatite* from material raw powder bone fish already cob _ calcined with precursor sour various phosphates . _ Based on results study This obtained results *Hydroxyapatite* which has mass different in accordance with treatment variation precursor sour phosphate . Optimum results obtained from synthesis *Hydroxyapatite* This that is on variation concentration sour 3M phosphate with mass The resulting *hydroxyapatite* as much as 2.56 gr with mark ratio Ca /P of 1.22. Besides That results SEM analysis shows morphology *Hydroxyapatite* results synthesis form details smooth which is not uniform .Calcium carbonate is material important in biomaterials that can taken from shell creature live . Calcium carbonate in shell shell can purified And become CaO for dental materials in form *Precipitated Calcium Carbonate* (PCC) (Yuliatun , 2023). PCC is product processing of natural materials containing calcium carbonate through series reaction chemistry .

On generally PCC is made through hydration of CO_2 (carbon dioxide). The resulting product colored white And have distribution size uniform particles (Maulia , 2020) . *Hydroxyapatite* have ratio calcium-phosphate or often known with ratio Ca /P. Based on ISO 13175 2015 standard mark ratio Ca /P hydroxyapatite that is of 1.67 (Henggu , 2019). Mark ratio Ca /P at *hydroxyapatite* will influential to strength mechanic *hydroxyapatite* with ratio critical Ca /P of 1.67. this _ because the more big ratio Ca /P then the resulting *hydroxyapatite* the more strong And reach mark maximum ratio 1.67. Besides That other properties *of hydroxyapatite* that is on its solubility Where relate with characteristic biocompatible with

network And reaction chemistry with compound other . Rate solubility This will influenced by difference shape , porosity , size crystals , crystallinity , and size crystallite from *hydroxyapatite* (Yusuf, 2019). In this study the aim was to obtain hydroxyapatite by means of synthesis using the sol-gel method.

II. METHODS

Material

Materials used _ is green mussel shell waste obtained from coast beach Kenjeran , Surabaya which will be later will processed especially formerly to PCC (*precipitated calcium carbonate*). H3PO4 _ _ _ (sour phosphate) is compound precursor used _ in run variable _ And NaOH (sodium hydroxide) is compounds used _ as alkaline pH regulator

Tool

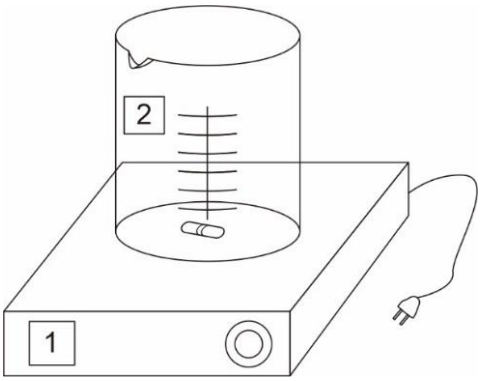

Fig 2. A Set of Magnetic Stirrers

Study This need tool form Suite a set of magnetic stirrer, beaker glass, pipette , spatula, glass measure , pumpkin measure , paper strain , funnel glass .

Procedure

1. Making PCC material from Waste shell Shell green

Wash raw materials Green mussel shell waste as much as 10 grams to remove adhering dirt using aquadest and alcohol. Grind the raw materials using a mortar and then sift using a 100 mesh sieve. Carry out the calcination process of green mussel shells using *a furnace* with a temperature of 9 0 0 ^{o} C for 2 hours. React results calcination shell shell green with HCl 2N as much as 100 ml . Test the pH of the mixture, if it is in an acidic environment, add the NaOH compound until the pH becomes alkaline. Add sodium carbonate (Na_2CO_3) 6N and stir using *a magnetic stirrer* at 300 rpm for 10 minutes. Filtration was carried out on ^{the} stirring results and then the precipitate of CaCO3 was taken $_{which}$ was filtered and carried out drying using an oven with a temperature of 10 0oC so that PCC was obtained from the waste green clam shell

2. Synthesis Hydroxyapatite (HAp)

Mix PCC with 50 mL of water then mixed with 50 mL of $H_3PO_{4\ solution}$ (0.1 M; 0.5 M; 1 M; 1.5 M; and 2 M) . Stir for 3 hours using a magnetic stirrer with a stirring speed of 300 rpm and the pH is maintained at pH 11 using the help of NaOH **.** Furthermore, the solution was aged (*aged*) at room temperature for 20 hours to form a gel **.** Filter the gel that has been formed use paper strain And part the filtrate was discarded **.** Heat the gel in the oven with temperature 105 ℃for 2 hours **.** The resulting powder then in the furnace at a temperature of 600 ^{o} C for 6 hours to form *hydroxyapatite* dry powder **. Perform** *Hydroxyapatite* powder analysis using AAS, FTIR, and SEM

III. RESULT AND DISCUSSION

On research that has done , product *hydroxyapatite* obtained _ Then done AAS (*Atomic Absorption Spectrophotometry*) analysis for know composition from element calcium And phosphate on product . Composition data second element the Then can made as base calculation For determine ratio Ca /P product the resulting *hydroxyapatite* . Based on AAS analysis that has been done obtained results as following :

Table 2. Result data Analysis of Calcium-Phosphate Levels along ratio Ca /P

Concentration of H_3PO_4	**Ca(wt%)**	**P(wt%)**	**Stamp**
0.1M	49.33	28.39	1.73
0.5M	49.1	28.79	1.7
1 m	48.85	29.15	1.67
1.5M	49.31	30.08	1.63
2M	49.28	30.52	1.61

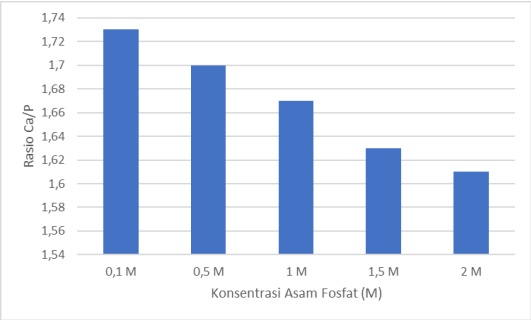

Fig 1. Concentration of Phosphoric Acid to Ca/P

Based on results AAS analysis on table 2 is known that mark a ratio close to ISO 13175 of 2015 exists on synthesis hydroxyapatite with variation concentration sour the resulting 1 M phosphate mark ratio 1.67. After done subsequent AAS analysis in a manner random sample chosen For analyzed using FTIR aiming For know existence group function hydroxyapatite.On analysis This obtained a number of group function main *hydroxyapatite* , yield the can seen as following :

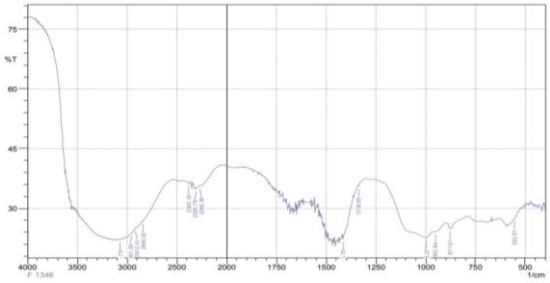

Fig 3. Results 1M Hydroxyapatite FTIR Testing pH 11

Based on the results of the FTIR test in Figure 2. Hydroxyapatite with a variable of 1 M pH 11 shows the presence of OH groups which indicated by the OH bond at the peak of 3068.75 cm^{-1} . The presence of PO bonds from FTIR analysis was detected at a peak value of 995.27cm^{-1} And it's very well known as the PO_4^{3-} group PO [13]. The presence of PO and OH^- bonding groups in the synthesized material confirms that it is hydroxyapatite, a compound with the chemical formula $Ca_{10}(PO_4)_6(OH)_2$, where PO_4^{3-} and OH^- are integral components of the hydroxyapatite structure.

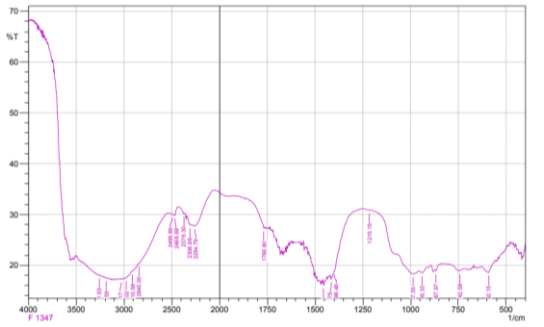

Fig 4. Results FTIR Testing of Hydroxyapatite 2M pH 11

Based on the FTIR test results in the picture above . *Hydroxyapatite* the best for the 2 M pH 1 1 sample , it can be seen that there is a PO_4^{3-} group on long wave 592.15 cm^{-1} ; besides That Also seen group OH function $^-$ on long wave 3261.63 cm^{-1} ; And For group function Ca -O is visible on long wave 1415.75 cm^{-1} ; 1454.33 cm^{-1} ; and 1766.8 cm^{-1} . From the results FTIR analysis is known that *hydroxyapatite* own

group function PO_4^{3-} ; OH- ; – And group function Ca -O. it _ show that study This has in accordance And can seen from study earlier by Kurniawan on in 2019 where the resulting *hydroxyapatite* there is bond PO_4^{3-} ; OH- ; – And Ca -O which is group function main from *hydroxyapatite* .From the results test 1M pH 12 and 2M pH 11 at 2M pH 11 exist group function Ca -O shows study This has appropriate . Influencing factors _ from results test that is on concentration sour which phosphate _ sour phosphate with concentration low will potentially big Still leaving precipitate calcium so that Still there is remainder possible phosphate _ form compound others (Oji, 2019) Furthermore sample analyzed use SEM for know morphology from formed crystals _ on product hydroxyapatite .

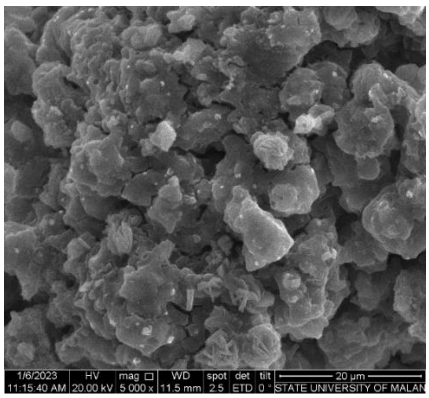

Fig 5. Results SEM analysis for Product Hydroxyapatite

Based on results SEM analysis is known morphology crystal *hydroxyapatite* formed _ is shaped *spherical* going to to granular and own distribution particles that don't equally as well as agglomerate . Based on research that has done by Daughter on 2016 p _ the Already in accordance with the results of the SEM carried out Where happening clumping particle on surface caused due to the mixing process during the synthesis process No perfect so that particle No spread evenly .

IV. CONCLUSION

From the results AAS analysis for concentration sour 0.1 M phosphate ; 0.5M; 1 M; 1.5M; and 2 M respectively obtained ratio calcium-phosphate (Ca /P) 1.73 ; 1.70; 1.67; 1.63; and 1.61. Results that are closest to ISO 13175 for ratio Ca /P Hydroxyapatite obtained on concentration of 1 M of 1.67. Besides That characteristics the resulting *hydroxyapatite* is known own group function main hydroxyapatite form PO_4^{3-} ; OH- ; – And group function Ca -O and form structure crystal *hydroxyapatite* is known shaped *spherical* , no evenly , and agglomerate .

V. ACKNOWLEDGMENTS

Researchers thank the participants who have taken part in this study. We also want to thank all the researchers who helped collect data for this research review.

REFERENCES

[1] Alpina,YZ(2017)'Synthesis *of Hydroxyapatite* from *Precipitated Calcium Carbonate*(PCC)of Chicken Eggshells Through the *Sol Gel Process* with Variations in pH and Aging Time', ***JOM FTEKNIK***, Vol.4,No.2, hh1 - 4

[2] Cappenberg, (2008) 'Some Aspects of Green Mussel Biology', *Oceana,* Vol.1, No.1, hh 33-40

[3] Kurniawan, HC (2019) "The Effect of Phosphate Concentration on Ca/P Ratio of Hydroxyapatite from Ceramic Industrial Gypsum Waste**", *journal MIPA Sciences* ,** Vol. 19, No. 1, pp . 46-56

[4] Liemawan , T. R (2015) ' Utilization of Green Mussel (Perna Viridis L.) Waste as a Mixing Material for Optimum Content of Fine Aggregate in Concrete Mix Design with the Substitution Method ', ***journal ITS Engineering* ,** Vol. 4, No. 1, hh . 128-133

[5] Maulia (2020) ' Making PCC (*Precipitated Calcium Carbonate*) Using Lime Ingredients _ *Mud* With Method Caustic Soda', ***Journal Vocational Technology Industry* ,** Vol2. No.2

[6] Mozartha, M (2015) ' *Hydroxyapatite* and Its Applications in Dentistry',***Cakradonya Dent Journal*** ,Vol.7,No. 2, hh807-868.

[7] Oji. P. (2019) Optimization Concentration Sour Phosphate in Making *Hydroxyapatite* From Waste Bone Fish Cob *(Euthinus Affinis)* with Method precipitation ", ***journal Chemistry*** , Vol. 1, No. ,1 , pp 1-7

[8] Putri, V., D. (2016) " Influence Ca /P Molar Comparison In Making Calcium Film _ Phosphate from Precursor Ca (NO_3) $_2$ .4H_2O Via Sol-Gel Method **", *journal Catalyst*** , Vol. 1, No. 2, hh 2-10.

[9] Sunarsih , (2014) ' Concept Processing Waste House Ladder in Effort Prevention Pollution Environment ', ***Journal Knowledge Health Society*** , Vol. 5, No.3, pp. 162-167

[10] Yuliatun , K. (2023) ' Making *Precipitated Calcium Carbonate* (PCC) from shell Shell through Dissolution , Carbonation , and Sonication ', ***Journal of Aceh Physics Society***, Vol. 12. No1, pp. 27-31

[11] Joseph. Y, et al 2019 *Hydroxyapatite Based on Biogenic* , Gajah Mada University Press, Yogyakarta