Synthesis of Hydroxyapatite Using Microwave Irradiation and Sintering with Variation pH and Time

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Abstract. Hydroxyapatite (HAp) with the formula of chemical compound $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ is a bone replacement material used in alternative bone graft technology. This study aims to analyze the effect of variations in pH and time on Hydroxyapatite synthesis using microwave irradiation and sintering. The results show variations in pH and time affect crystal size, degree of crystallinity and morphological forms. XRD characterization showed that the samples irradiated by microwaves with time variations produce a crystal size of around 15 until 21 nm. The addition of the sintering process results in three times the crystal size be compared to the microwave process. XRD characterization also shows that variations in pH give rise to a secondary phase in the form of chlorapatite. FTIR characterization shows that the sintering process removes carbonate groups and SEM-EDX characterization of pH 11 samples which are only irradiated by microwaves produces a particle size of about 63.43 nm with a Ca / P ratio of 1.59 and the addition of the sintering process produces a particle size of around 180.62 nm with a Ca / P ratio of 1.48. The use of high temperatures affects the growth of crystals in the synthesis of Hydroxyapatite.

Keywords: Hydroxyapatite, microwave irradiation, pH and sintering

1. Introduction

Bones are composed of 30% organic compounds and 70% inorganic compounds [15]. Eight million people experienced fractures with different types and causes according to the Ministry of Health in 2013. The high number of fracture cases has triggered a lot of research to develop alternative technologies for bone grafts to treat fractures. Calcium phosphate used by some researchers is hydroxyapatite with the formula of the chemical compound $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ [13]. Hydroxyapatite has a chemical structure similar to bone structure, so it is good for bone graft material [7]. Although Hydroxyapatite has a similar chemical structure to human bones, the mechanical performance of Hydroxyapatite is still very low compared to human bones. Thus, it is necessary to increase some of the Hydroxyapatite properties by controlling several important parameters such as particle size, particle shape, and agglomeration which can improve the quality of Hydroxyapatite [16].
Control variables that are often used by researchers are pH, temperature, type of reactants, the concentration of binding, length of synthesis time and reaction rate [12]. In previous studies, pH was a significant parameter variable in looking at morphology [10] and sintering was a parameter that was successfully used to grow crystal size in Hydroxyapatite [17]. The purpose of this research is to produce Hydroxyapatite using microwave irradiation methods with time variations and the addition of the sintering process, analyze the effect of pH variation on Hydroxyapatite synthesis and analyze the effect of microwave irradiation and sintering methods.

The use of microwaves to reduce losses by conventional methods. Microwave heating, heat sources originating from samples and heat generated from internal materials do not originate from external heating [15]. This heating is caused by dipolar polarization of polarized molecules due to chemical bonds and the presence of high frequency electric fields. High frequencies result in molecular internal friction which will lead to volumetric heating of the material [4,5,6]. Sintering is a processing technique used to produce materials by controlling the density of materials using thermal energy which aims to control microstructural materials such as increasing particle size and controlling the distribution of phases formed in materials such as the formation of pores [4].

2. Materials and Methods
The material used in the synthesis of this study uses Merck labeled chemicals such as Ca(OH)\(_2\) with a concentration of 1 M, (NH\(_4\))\(_2\)HPO\(_4\) with a concentration of 0.6 M, 1 M HCL solution to reduce pH and 1 M NaOH solution to increase pH.

2.1. Synthesis of HA with microwave irradiation and sintering
Hydroxyapatite synthesis used two solutions, a solution of Ca(OH)\(_2\) as a precursor of calcium and solution (NH\(_4\))\(_2\)HPO\(_4\) as a phosphate precursor. Both of these solutions are mixed with titration using a burette by giving a drop rate (5 mL/minute). After the solution is mixed, the solution is made in two conditions, the solution is controlled by variations in pH, namely pH 7, 9, 11 and is not controlled by pH. In a controlled solution with pH, the solution is added with HCl to obtain a pH value of pH 7 and 9 and a NaOH solution to obtain a pH value of 11. The sample is inserted into the microwave to be irradiated using microwaves with a variation of time between 15, 20 and 25 minutes. After irradiation using microwaves, the sample is filtered, so that only sediment is used. The sample is put into the oven to dry. Then the dried sample is crushed using a mortar to become powder. Furthermore, sample powder was sifted using mesh with the size of 100 nm and characterized by XRD, FTIR, and SEM-EDX. The addition process is sintering at 900\(^\circ\)C for 5 hours and then after sintering process, the sample is characterized again.

2.2. Characterization of HA
This research characterization using XRD, FTIR, and SEM-EDX. XRD characterization is used to determine the crystal size, degree of crystallinity and lattice parameters and the tool used is PANalytical: X’Pert PRO. FTIR characterization using Thermo Scientific tools and Scanning Electron Microscope (SEM) using tools that name the tool (FEI, QUANTA 650) and for EDX used Aztec Oxford Instruments.

3. Result and discussion
3.1. XRD analysis
The results of characterization using XRD are shown in Figure 1. The three images show an increase in irradiation time resulting in an XRD pattern with insignificant differences between one sample and another at the same pH value. Figure 2a is a graph of the variation of pH with crystal size (L) and Figure 2b graph between variations in pH with CI in three variations of time 15, 20, and 25 minutes. The graph formed is in line with the results of the XRD pattern, a significant increase occurred at the time of 25 minutes irradiation by the results of the calculation of crystal size and a high degree of crystallinity. The
time variation used is only 15 until 25 minutes because if more than 25 minutes of the hydroxyapatite sample is scorched. The length of irradiation time increases crystal size and the degree of crystallinity in all samples. The diffusion process of atoms that are influenced by external sources is the microwave irradiation causes the atoms to vibrate rapidly so that it is increasing the temperature. High temperatures cause the atoms to move through diffusion so that they are easily bonded and enter the lattice parameters to increase the degree of crystallinity [3].

![Figure 1](image1.png)  
**Figure 1.** XRD patterns of HA which exposed in MW (a) for 15 minutes, (b) for 20 minutes and (c) for 25 minutes

![Figure 2](image2.png)  
**Figure 2.** (a) Graphic size of HA crystal samples with variations of time and (b) Graphic of the crystallinity of HA samples with a time variation

![Figure 3](image3.png)  
**Figure 3.** (a) The XRD HA pattern with the effect of variations in pH 7, 9 and 11 on irradiation 25 minutes and (b) The XRD pattern irradiation MW and sintering with variations pH on irradiation 25 minutes
The effect of pH variation in hydroxyapatite synthesis is very clearly seen with the results of the XRD produced. The results of Hydroxyapatite XRD synthesized by microwave irradiation at 25 minutes with pH variations are shown in Figure 3a. It shows the XRD pattern produced in samples with pH 7 and 9 having XRD patterns that are different from HA controls, resulting in peaks with the maximum intensity found at hkl (300). The effect of sintering is affecting the XRD pattern that results from variations in pH found in Figure 3b. The XRD pattern produced in samples pH 7 and 9 only produce two peaks, when matched with the database using the high score show the highest score is chlorapatite while the Hydroxyapatite score is low. The changes in HA to CIA at pH 7 and 9 due to the addition of hydrochloric acid (HCl) and sintering at high temperatures of 900°C. In addition to hydrochloric acid makes Cl-ions substitute OH- so that CIA forms with water [10]. The formation of the XRD pattern, which is similar to pH 7 and 9 samples, shows the resulting morphology in the form of a needle as in Zhang (2011).

3.2. FTIR analysis
Figure 4a shows the results of FTIR spectrum in HA samples with variations in pH without sintering. From the picture, it can be seen that in HA samples with pH 7 and 9, there is a functional group (CO$_3^{2-}$) getting sharper when the pH value gets lower. The presence of functional groups (CO$_3^{2-}$) originates from the atmosphere absorbed during the synthesis process [16]. The effect of sintering on FTIR spectrum results on HA samples with pH variations is shown in Figure 4b. It shows the effect of the sintering is widening the peak of the (OH-) and removing the group (CO$_3^{2-}$). Table 1 present the wavenumber of HA only irradiation MW and irradiation MW and sintering. The stretching that occurs in water groups because water is being absorbed during the synthesis process and adsorbed to the surface. In the control HA sample and HA with pH 11, there were groups (OH-) in the range of 630 cm$^{-1}$. HA samples with pH 7 and 9 groups (OH-) in the range of 630 cm$^{-1}$ none, this is because (OH) ions are substituted with chloride ions derived from hydrochloric acid. However, the widening of the peak in the group (OH-) is due to the absorption of water molecules against HA particles and the influence of high temperatures [9,14,16].

Figure 4. (a) FTIR spectra of HA only irradiation MW for 25 minutes and (b) FTIR spectra of HA irradiation MW and sintering for 25 minutes
Table 1. Characteristic infrared bends for HA irradiation MW and sintering

| Functional Group | Wave Number (cm) | Wave Number (cm) |
|------------------|------------------|------------------|
| V<sub>1</sub> PO<sub>4</sub><sup>3-</sup> | 961 960 961 | 962 962 962 |
| V<sub>2</sub> PO<sub>4</sub><sup>3-</sup> | 472 474 472 | 471 473 473 |
| V<sub>3</sub> PO<sub>4</sub><sup>3-</sup> | 1022 1016 1013 | 1017 1012 1012 |
| V<sub>4</sub> PO<sub>4</sub><sup>3-</sup> | 560 556 556 | 560 561 557 |
| V<sub>2</sub> CO<sub>3</sub><sup>2-</sup> | 874 872 874 | 1418 1401 1417 |
| OH<sup>-</sup> librational mode | - - - | 630 - - |
| OH<sup>-</sup> stretch | 3561 3407 3402 | 3570 3408 3402 |

3.3 SEM - EDX analysis

The morphological form of HA samples with pH 11 power of 540 W at 25 minutes characterized using SEM shown in Figure 5a. It shows that some particles tend to agglomerate and the shape of the particles appears irregularly rounded. Irregularities due to particles formed are still amorphous. Amorphous properties are also blinded by the size of the crystals formed measuring around 16.72 nm and particle size was calculated using ImageJ software around 63.43 nm. The Ca / P ratio is 1.59. The effect of sintering on morphological forms is shown in Figure 5b, which results in more crystalline particles with round characteristics and tend to be still agglomerated. The shape of particles is produced according to the study [1, 8] which results in the form of round particles at alkaline pH. The particle size produced around 180.62 nm is calculated using ImageJ software and for a crystal size of around 60 nm. The crystallite size in the sintering sample produces a crystal size three times greater than the non-sintering crystal size. The Ca / P ratio produced is 1.48. The sintering has an effect on crystal growth. Temperature and pH are influential factors in the form of morphology. Temperature influences the increase in crystal size and forms more crystalline particles [2] and pH is the most significant influence in particle form [11].

Figure 5. (a) Morphological HA pH 11 form irradiated by microwave with a power of 540 Watt for 25 minutes at 50,000X magnification, b) Morphology of HA pH 11 sintering with 540 Watt power for 25 minutes at 50,000X magnification
4. Conclusion

Research synthesis Hydroxyapatite using microwave irradiation and sintering methods with variations in pH and time resulting in varying particle sizes, degree of crystallinity and morphological. Variations time between 15 until 25 minutes produce the highest average particle size in 25 minutes. The use of high temperature sintering method produces XRD spectrum with clear peaks and the effect of sintering on pH variations knowing that at pH 11 is a pH that is not much different from HA and at pH 7 and 9 chlorapatite is formed.

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