The effect of time and number of balls on shaker milling process in hydroxyapatite powder synthesis

A Fadli, S R Yenti, R Rasyidin, M Sari
Department of Chemical Engineering, Engineering Faculty, University of Riau
Kampus Bina Widya HR Subrantas Km 12.5, Panam, Riau Indonesia
fadiunri@yahoo.com

Abstract. The synthesis of hydroxyapatite (HA) from the shells of blood clams has been successfully performed by the low temperature hydrothermal method. To obtain uniform and nano-HA powder, size of obtained HA was reduced using shaker milling process. The purpose of this research was to determine the effect of time and the number of balls on the shaker mill process on hydroxyapatite particle size. The shells of blood clams were calcined at 1000 °C for 24 hours to obtain CaO powder. Then 55.63 gram (NH₄)₂HPO₄ dissolved in 600 mL of distilled water then added 45.91 gram of CaO at 90 °C to form slurry. The slurry was dried at 120 °C for 15 hours, and milled using shaker milling process with variation of time 1, 2 and 4 hours and variation of number 10, 20, and 30 balls. The peak intensities show the high percentage of HA with Tricalcium phosphate (TCP) presence in X-ray diffraction (XRD) analysis. Diameter of crystal produced is 67 nm, with time variation for 2 hours and number of 20 balls. Breuner-Emmet-Teller (BET) analysis result, with time ball milling for 1 hour and the number of 10 balls surface area of HA is 36.974 m²/g. The longer of milling process, the temperature will also increase causing clumps of particles resulting in an increase in particle size. The more the ball is used then the surface area of obtained hydroxyapatite will be smaller.

1. Introduction
Heavy metals generally refer to its density greater than 5 g/cm³ with biological toxicity. Such as silver (Ag), copper (Cu), lead (Pb), zinc (Zn), nickel (Ni), tin (Sn), cadmium (Cd), chromium (Cr), mercury (Hg) and metalloid such as arsenic (As). Without appropriate treatment, industrial wastewater, urban sewage and agricultural production wastewater bring the most heavy metal pollution into the natural water bodies and caused one of the most serious globe environmental problems [1]. The heavy metal can be accumulated into the food chain and cause serious problems, not only for the ecosystems but also for human health [2].

Several methods have been used in the removal of heavy metal involve physical (filtration, coagulation, adsorption), chemical (ion exchange, adsorption) and biological processes. Adsorption is the technology most commonly used to reduce heavy metals from waters. This method is often used because the price is relatively cheap, environmentally friendly and simple to do. The most important part in an adsorption process is the type of adsorbent that will used [3]. HA can act as an ion removal material due to its excellent reactivity and low water solubility [4]. HA can be synthesized through various methods, including hydrothermal [5], precipitation [6], sol-gel [7] and mechanochemical methods [8].
Hydroxyapatite (Ca$_{10}$(PO$_4$)$_6$(OH)$_2$), a major inorganic constituent of vertebrate hard tissues such as bone and tooth, due to its excellent bioactivity, biocompatibility and osteoconductivity. HA also considered as one of the most promising mineral phases for remediation of polluted waters and soils, sorption of organic molecules and heavy metal ion removal. HA has strong affinity to their surface for cationic species [9].

In the application of HA as an adsorbent, the morphology and particle size become important parameters. Micro-HA has small surface area and has a strong crystal bond so it is good to be used as an adsorbent. To get small HA particle size, several studies have been conducted using ball milling technique. Wu et al. [10] used eggshell as the source of Ca, was combined with Dicalcium phosphate dehydrate (DCPD) powder. The powder mixture was ball-milled for 1, 5 and 10 h followed by heat treatment at 1000°C for 1 h. The formation of HA phase can be initiated by sintering the 1 h milled at 1000°C for 1 h, while pure HA phase can be obtained upon sintering the 10 h milled sample. Hamidi et al. [11] used eggshell as raw material to synthesize eggshell-derived HA (EHA) via mechanochemical method. HA powder was successfully synthesized with crystallite and particle sizes in the range of 8-47 nm and 250-550 nm respectively. Gergely et al. [12] synthesized HA used seashell and eggshell, the crushed and milled in ball mill or an attritor mill. The characteristic morphology is preserved even after firing at high temperature (900°C). After heat treatment HA, calcium oxide and calcium phosphate phases appeared. In this research, ball milling technique was used to obtain smaller HA size, with variations in the number of ball and grinding time.

2. Materials and Method

2.1. Materials

The clam blood shells were collected from the local market at Pekanbaru, Riau Indonesia. Ammonium dihydrogen phosphate as the source of phosphate and distilled water was used.

2.2. Methodology

The clam shells were cleaned with water, dried and crushed into powder. The powders were then calcined in a furnace at 1000°C for 24 h. The calcination aimed to decompose calcium carbonate (CaCO$_3$) into calcium oxide (CaO) which will be used as Ca precursors. The results were then tested using Atomic Absorption Spectrometer (AAS) to measure calcium content in a sample. The calcium data from the AAS test were used for stoichiometric calculations to find the mass of CaO will be used in the HA synthesis process. This process performed is carried out using a low temperature hydrothermal method which refers to the research of Alqap and Sopyan [13].

Calcinated shells 45.91 gr were mixed with 55.63 gr of ammonium dihydrogen phosphate and distilled water 600 ml. The solution was heated at 90°C and stirring at 300 rpm for 5 h. The slurry were then dried at 120°C for 15 h. The dried samples were then milled to get a smaller size using a shaker ball mill with variation of the number of grinding balls 10, 20 and 30 balls and grinding times of 1, 2 and 4 h. Samples then calcined at 900°C for 2 h at a rate 10°C/min. CaO levels were analyzed using AAS. The crystalline phase of clam blood shells before and after the calcination were analyzed using powder X-ray diffraction (XRD). The microstructure and morphology of the powders were observed using scanning electron microscope (SEM). Particle Size Analyzer (PSA) and Brunauer-Emmet-Teller (BET) were used to determine the distribution of sample particle size and the sample surface area.

3. Results and Discussion

HA was synthesized from blood clam shell as source of calcium. Calcium derived from Calcium oxide (CaO) produced by calcination of clam shells at 1000°C for 24 h. The percentage of CaO levels obtained was 76.2 based on dry weight. The XRD analysis showed that the clam shells before the
calcination were CaCO$_3$ phases, which had the highest peak and the calcined process turned clam shells into CaO phases. Calcium oxide can be obtained as follows:

$$\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$$

(1)

![Figure 1. X-ray diffraction of clam blood shells (a) before calcination (b) after calcined at 1000°C](image)

The XRD analysis showed that the clam shells before calcination had the highest peak of CaCO$_3$. The calcined shells turned into phases of CaO which was the highest peak at angle 2θ 35°. From the graph of XRD analysis for the sample after calcination showed crystal peaks or head of CaO as shown in Figure 1.

Based on the XRD analysis results of ball milling samples, HA phase were formed with hexagonal crystalline structure, besides that a Tricalcium phosphate (TCP) phase was formed with rhombohedral crystal form as shown in Figure 2. The HA peaks for the sample (ball milling 4 h 30 grind balls) at 20 i.e 25.877°, 32, 162°, 43.845°, 53.205° and 61.6653°. The XRD patterns showed the similarity with the JCPDS file no. 09-0432.

Ball milling samples were calcined at 900°C, there was no CaO phase at this calcination temperature. In the sample, the composition contained was HA and TCP. CaO which was still present in the sample cause the formation of TCP [13].
Figure 2. XRD analysis of HA powder at 900°C calcination temperature

The sample also characterized by SEM analysis, which is used to determine the morphology of the sample. The SEM images showed that the powder is smooth and uniform, there is no agglomeration and form the same pore.

Figure 3. SEM analysis of HA powder after calcination at 900°C

3.1. Effect of Ball Milling Time
During the ball milling process, HA particles would be repeatedly milled. When the balls were milled, the powder will be trapped between them. The load given by the milled balls to the powder will make the plastic deformed so that it undergoes hardening and finally grinded.
Figure 4. PSA graph particle size distribution of HA using 20 balls with different time (a) 1h (b) 2 h and (c) 4 h

From the results obtained by using the same number of grinding balls at 1, 2 and 4 h it can be seen that 2 h of grinding time, the size of HA particles has the smallest size. HA particles size using 20 ball mill at 1 hour was 74.3 nm, while at 2 h the size of HA particles obtained was 67 nm and at 4 h HA particle size was 110.3 nm. The increasing of milling time also increases the milling temperature so the contaminant can occur in HA powder. The crystalline size of HA from clam blood shells was calculated using the Scherrer’s equation and shown in Table 1.

| Time (h) | Number of balls |
|---------|----------------|
|         | 10             | 20            | 30            |
| 1       | 187 nm         | 74.3 nm       | 117.4 nm      |
| 2       | 166 nm         | 67 nm         | 83.4 nm       |
| 4       | 438.9 nm       | 110.3 nm      | 217.1 nm      |
After 2 h, the enlargement of particle size occurs. This occur as a result of the cold-welding rate was higher compared to rate of grinding by ball mill. After 2 h, the cold-welding rate and the rate of grinding of the powder has reached the equilibrium limit. To overcome this, a process control agent can be added to the grinding process and the powder will be covered and reduced the influence the rate of cold welding which results of powder particles agglomeration [14].

3.2. Effect of number of ball mill
The effect of the number of mill balls on the particle size obtained is seen at each milling time. At each milling time, the smallest particle size was obtained when using the number of 20 mill balls. Particle size reduction using ball milling will be maximal when the ball milling is filled with ball and the sample to be milled is not more than 50% of the volume of the shaker ball mill.

**Figure 5.** PSA graph of HA at 1 h milling time (a) 10 mill balls (b) 20 mill balls (c) 30 mill balls
Table 2. Effect of time and number of mill balls on HA surface area

| Time (h) | Number of balls | Surface Area (m²/g) |
|---------|-----------------|---------------------|
| 1       | 10              | 36.974              |
| 1       | 30              | 1.359               |
| 4       | 30              | 3.071               |

BET analysis was also used in this study. This analysis was conducted to determine the sample surface area. Based on table, with the same ball milling time of 1 h using 10 and 30 grinding balls obtained smaller surface with the increasing number of balls, which were obtained by milling of HA powders with 10 and 30 balls were 36.974 and 1.359 m²/g. Whereas ball milling using the same number of grinding balls as 30 balls at 1 and 4 h of grinding time, surface area increase with increasing time. The surface area of HA powders using 30 balls at 1 and 4 h were 1.359 and 3.071 m²/g.

4. Conclusion

Ball milling is simple and efficient method to produce micro or nano powder particles. The time and number of milling balls that produce the smallest HA particle size is 2 h and 20 mill ball with HA particles size used 20 ball mill at 1, 2 and 4 h were 74.3, 67 and 110.3 nm. The increasing of milling time and number of milling ball, the reduction of particle size of HA also increasing. The surface area HA will increase with the smaller size of HA. Milling process of HA powders with 10 and 30 balls, the surface area were 36.974 and 1.359 m²/g. The ball milling used 30 balls with different time 1 and 4 h, the surface area were 1.359 and 3.071 m²/g. However, the use of time and number of balls in ball milling process must be adjusted to the efficiency of the ball mill used.

Acknowledgements

The authors are grateful for the financial supports from Riau University for the financing of this research through 2018 Competitive Grant scheme.

References

[1] Hao C, Anbin X and Shaohong Y 2018, IOP Conf. Series: Mater. Sci. Eng 301 012160
[2] Abbasi Z and Aghababaei M 2014. Universal Journal of Engineering Science 2 124
[3] Mourabet M, El Rhilassi A, El Boujaady H, Bennani-Ziatni M, El Hamri R, Taitai A 2012 Applied Surface Science. 10 4402
[4] Avram A, Frentiu T, Horovitz O, Mocanu A, Goga F, Tomoaia-Cotisel M 2017. Studia Universitatis Babes-Bolyai, Chemia. 162.
[5] Sopyan I and Kaur J 2009. Ceramic International 35 3161
[6] Cox SC, Jamshidi P, Grover LM, Mallick KK 2014. Journal of Materials Science: Materials in Medicine 25 37
[7] Bezzi G, Celotti G, Landi E, and La TMG 2002. Materials Chemistry and Physic 78 816
[8] Rhee, S 2002. Biomaterials 23 1147
[9] Yang H, Masse S, Rouelle M, Aubry E, Li Y., Roux C, Journaux Y, Li L. and Coradin T 2015. International journal of environmental science and technology, 41173
[10] Wu SC, Hsu SH, Hsu SK, Chang YC, and Ho WF 2015. Journal of Asian Ceramic Societies
[11] Hamidi AA, Salimi MN, and Yusoff AHM 2017. Advanced Materials Engineering and Technology V
[12] Gergely G, Weber F, Lukacs I, Illes L, Toth AL, Horvath ZE, Mihaly J, and Balazs C 2010. Central European Journal of Chemistry 8 375
[13] Alqap SF, and Sopyan I 2009. Indian Journal of Chemistry 48 1592
[14] Suryanarayana, C 2001. Progress in Materials Science 46 1