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Preparation and Characterization Nanoparticle Calcium Oxide from Snakehead Fish Bone using Ball Milling Method

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Abstract

Snakehead Fish Bone (SFB) is a waste from food processing in Palembang. Fish bones have calcium content so they have a potential as a source of Calcium Oxide (CaO). Calcination of fish bones was carried out at a temperature of 900°C with variations of time 1, 2, 3, and 4 hours. The Nanoparticle Calcium Oxide (NCO) was prepared using the ball milling method. This study aims to make NCO as a raw material for hydroxyapatite synthesis. The NCO was characterized using *Fourier Transform Infra-Red* (FTIR), *X-Ray Diffraction* (XRD), and *Scanning Electron Microscope* (SEM). Characterization using FTIR shows that NCO has functional groups O-H, CO_3^{2-} and PO_4^{3-} functional groups. XRD analysis shows that NCO has an average particle size of 38.9445 nm. Analysis using SEM shows particles in the form of granules of almost uniform size. The NCO produced eligible of the nanomaterial and has the potential as a raw material for synthesis of hydroxyapatite.

Keywords: Nanomaterial, ball milling, calcium oxide, fish bone

Abstrak (Indonesian)

Tulang ikan gabus (SFB) merupakan limbah dari pengolahan makanan di Palembang. Tulang ikan memiliki kandungan kalsium sehingga berpotensi sebagai sumber Kalsium Oksida (CaO). Kalsinasi tulang ikan dilakukan pada temperatur 900°C dengan variasi waktu 1, 2, 3, dan 4 jam. Nanopartikel Kalsium Oksida (NCO) dipreparasi menggunakan metode ball milling. Penelitian ini bertujuan untuk membuat NCO sebagai bahan dasar untuk sintesis hidroksiapatit. Karakterisasi dilakukan menggunakan *Fourier Transform Infra-Red* (FTIR), *X-Ray Difrraction* (XRD), dan *Scanning Electron Microscope* (SEM). Karakterisasi menggunakan FTIR menunjukkan NCO memiliki gugus fungsi O-H, CO_3^{2-} dan PO_4^{3-}. Analisis XRD menunjukkan NCO memiliki ukuran partikel rata-rata 38,9445 nm. Analisis menggunakan SEM menunjukkan partikel berbentuk butiran dengan ukuran yang hampir seragam. NCO yang dihasilkan memenuhi syarat nanomaterial dan berpotensi sebagai bahan dasar pembuatan hidroksiapatit.

Kata Kunci: Nanomaterial, ball milling, kalsium oksida, tulang ikan

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INTRODUCTION

South Sumatra in particular the city of Palembang has various types of typical foods including pempek, kemplang, models, tekwan, and others. Snakehead fish is a fish that is widely used in processed foods. Fish bones have the most calcium content from the fish body [1]. Generally, fish bones are a by-product [2] or unused waste because the texture is hard and difficult to mash. It would be better if this waste converted into a material that is useful and has economic value.

Several research has been conducted to increase the economic value of fish bone waste, for example fish bone flour [3, 4], gelatin [2], and hydroxyapatite production [5-10].

Fish bones have major mineral components (60-70 g / 100 g) and collagens (~ 20 g / 100 g) [11]. snakehead fish bone (SFB) have protein content

(15.49%), lipids (4.19%), ash (32.05%), and moisture (43.19%) [12]. SFB have calcium content around 16.86-22.77% [13]. The calcium content in fish bones has the potential as a base for the synthesis of calcium oxide (CaO).

CaO can be made from various materials such as chicken bones [14], eggshells [15], beef bone [16], *Lates calcarifer* [7], and blood clams [17]. CaO can be used as a catalyst for biodiesel production [17], and the raw materials for hydroxyapatite synthesis [18].

Nanoparticles are compounds with a nanometer scale. The general agreement of nanometer dimensions is a size that is less than 100 nm [19]. Nanoparticles have different properties and characteristics compared to the same compound in the bulk size. Ball milling is one method in synthesis nanoparticle. This method was chosen because it does not require hazardous chemicals in the process. This method has the principle of shrinking particle size by grinding to nanometer size. The ball milling method has been widely used in research, such as milling of porang flour [20], synthesis of Nano crystalline graphene/Ni composite [21] and starch nanocrystals preparation [22]. The wet ball milling method used for the nano fish bone (NFB) preparation. NFB preparation results have an average particle size of 115 nm with operating conditions with a speed of 3000 rpm and a ball diameter of 0.5 mm [23].

In this study, CaO was obtained from the calcination of SFB powder with a time variation. CaO from calcination is then converted into nanoparticle calcium oxide (NCO) using the ball milling method. Characterization of NCO includes particle size analysis using XRD, functional group using FTIR and morphology using SEM.

MATERIALS AND METHODS

Materials

The chemicals used are analytical grades such as HCl, $SrCl.6H_2O$, H_2O_2 (was supplied from Merck) and aquadest. SFB was collected from Km 5 traditional market at Palembang city.

Preparation of NCO

The SFB is cut with a size of ± 2-5 mm as much as 1 kg boiled for 1 hour then washed and dried in the sun to dry (constant weight ± 1 day). A 100 g of SFB macerated with a solution of 1 M HCl for 2 hours, then washed to neutral pH and dried in an oven with a temperature of 105°C for 2 hours. Dried SFB was crushed using mortal then filtered 60 mesh and stored in a desiccator. SFB destruction is carried out according to the procedures of SNI 06-6989.56.2005.

SFB powder was calcined in a furnace at a temperature of 900°C for variations of time 1, 2, 3, and 4 hours. CaO powder from calcination is smoothed using a *High Energy of Milling* (HEM), for 1 hour with a weight ratio of CaO: a ball is 1: 5.

Analysis Data

Particle size can be determined using *Scherrer's* equation shown in equation 1.

$$d = \frac{0{,}9\,\lambda}{FWHM\cos(\theta)} \qquad (1)$$

Where d is the particle size, λ is the X-ray wavelength and θ is the Bragg angle.

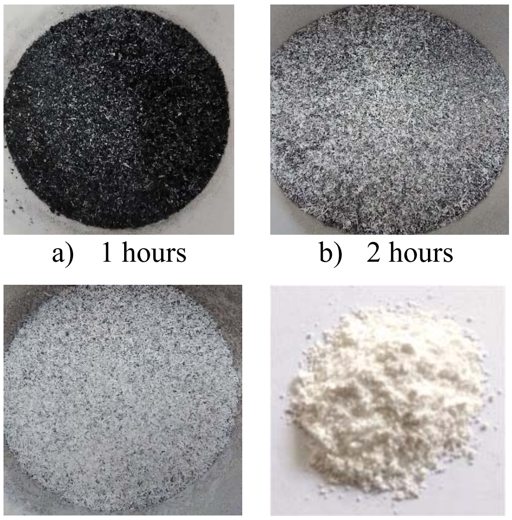
RESULT AND DISCUSSION

Analysis of Calcium Content

Before being analyzed using *Atomic Absorption Spectroscopy* (AAS) AA-7000 Shimadzu, the sample was first diluted using $SrCl_2.6H_2O$ 1% solution which aims to reduce matrix disturbances when analyzing. The analysis shows that SFB has a calcium content of 39.836%. This result is higher than the results of previous studies which obtained an average calcium level of 16.86% - 22.77% [13].

Characteristics of CaO

Calcined SFB powder at high temperatures aims to decompose organic compounds in SFB. The calcination process is carried out at a temperature of 900°C for 1 to 4 hours. Figure 1 shows the CaO calcined from SFB.



a) 1 hours b) 2 hours

c) 3 hours d) 4 hours

Figure 1. CaO Powder from SFB

Figure 1shows black powder obtained at 1 hour calcination time. When the calcination time is added to

2 hours the colour becomes dark grey and becomes light grey when the calcination time is 3 hours. A white powder obtained at 4 hours calcination, this shows it is CaO [18]. This white powder indicates the removal of organic compounds in SFB due to the calcination process [5]. The decomposition reaction is shown in equation 1

$$CaCO_{3\,(s)} \rightarrow CaO_{\,(s)} + CO_{2\,(g)} \quad (1)$$

Characteristic of SFB and NCO Using FTIR

The functional group of NCO was determined by using FTIR Thermo Scientific Nicolet iS10. In this study, the identification of functional groups was carried out at a wavenumber of 500-4000 cm^{-1}. Preparation of NCO was using ball milling method. The instrument used is *High Energy of Milling* (HEM). The milling process is carried out for 1 hour using tubes and balls made of teflon. The principle of this method is to destroy a particle up to nanometer in size. The spectra of SFB and NCO are shown in figure 2.

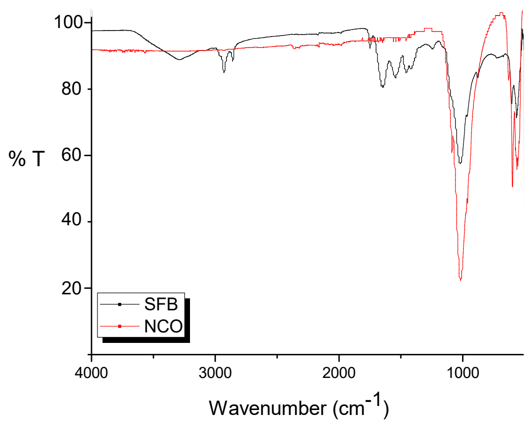


Figure 2. FTIR Spectra of SFB and NCO

Black lines show FTIR spectra from SFB. The O-H function group is shown at wave number 3282.20 cm^{-1}. Strong peaks in this area are characteristic of CaO [24]. Water molecules adsorbed on the surface of CaO cause this strong O-H group. CaO is hygroscopic so it is very easy to absorb water from the air [14]. The peak at wavenumber 1644.27 cm^{-1} indicates the O-C-O stretching of the CO_3^{2-} functional group which is reinforced by a peak at 1015.04 cm^{-1}. At wavenumbers 2922.88 and 2852.75 cm^{-1} indicate the functional group CH_2-NH_2 (primary amine) which is reinforced by a peak at 598.56 and 559.11 cm^{-1}. This amine function group shows samples containing amino acids. The results of Rosmawati's research show that SFB contains 17 kinds of amino acids [12].

Red lines show FTIR spectra of NCO. The wavenumber of 1019.71 cm^{-1} indicates the CO_3^{2-} functional group. The wavenumber of 598.60 and 563.26 cm^{-1} indicate the functional group PO_4^{3-}. The peak at almost the same wavenumber was also obtained in a bovine bone sample. This shows the sample has the potential as a raw material in the synthesis of hydroxyapatite [25].

Characteristic of NCO using XRD

The XRD spectra of NCO can be seen in Figure 3. Characterization using XRD is used to ensure the CaO obtained has a nanometer size. The spectra from characterization using XRD were matched with the *Joint committee on Powder Diffraction Standards* (JCPDS) pure CaO diffraction pattern. JCPDS No. 431-01 CaO fraction is characterized by the main peak in area 2-Theta 32.208; 37.360; 53.859; 64.157; 67.377 and 91.462. The XRD spectra with narrow peaks and high intensity show that the compounds formed have high crystallinity [26].

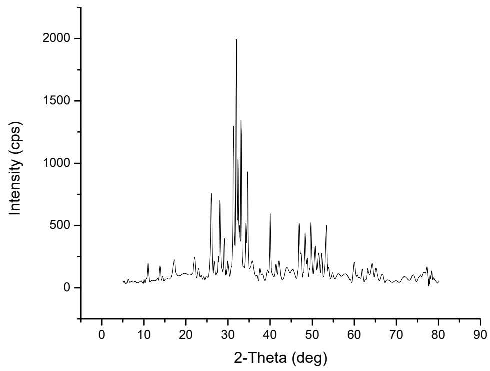


Figure 3. XRD spectra of NCO

The characterization of NCO using XRD Rigaku Miniflex 600 obtained an average particle size of 38.9445 nm, this indicates that the samples obtained qualify as nanomaterials.

Characteristic of NCO using SEM

The NCO morphology was determined using SEM JEOL JSM 6510-LA. The morphology of the NCO was observed at 40,000x magnification with a voltage of 15 volts and vacuum operating conditions. Figure 4 shows the SEM results of the NCO.

Based on this picture, we can see that the NCO particles are in almost uniform size granules. The picture also shows that the possible fibres are collagen. Collagen has tissue characters that are shaped white fibres, which are arranged irregularly [27].

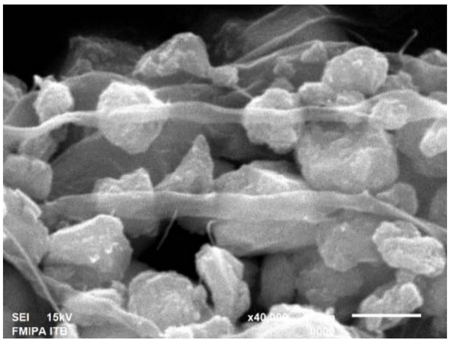


Figure 4. SEM of NCO with 40,000x magnification

CONCLUSION

CFB has a high calcium content of 39.836% so that it has the potential to be a source of CaO. CaO is formed at 4 hours of calcination time. The NCO obtained eligible the requirements as a nanomaterial and has the potential as a raw material in hydroxyapatite synthesis.

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