Time and Amplitude Effect on Nano Magnesium Oxide Synthesis from Bittern using Sonochemical Process

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Abstract. Magnesium in nature can be found in the form of minerals and seawater. Bittern is a sea-salt industry by-product that contains magnesium and potassium salts. Usually, bittern is discharged back to the sea, even though bittern can be further processed to obtain magnesium contained in it. Magnesium oxide (MgO) nanoparticles can be used in a variety of applications because of their good surface recreation properties. In this study, precipitation of Mg²⁺ ions from bitterns was carried out using sodium hydroxide to produce magnesium hydroxide. Then, it was calcined and went through sonochemical process to produce nano magnesium oxide. Sonication time and amplitude were used as variables. Sample with sonication time of 16 minutes and amplitude of 30% has the smallest particles with an average diameter of 195.7 nanometers.

1. Introduction

Magnesium oxide nanoparticles can be used in wide applications such as sensors and bactericides because of their good surface reactivity. It can be used as a humidity sensor due to its sensitivity to water vapor adsorption [1]. As a bactericide, superoxide ions are produced on the surface of magnesium oxide nanoparticles so that they can react with peptide bonds in bacterial cell walls or spores and destroy it. This bactericidal activity increases with decreasing of magnesium oxide particle size. Compared to titanium oxide nanoparticle which requires light, magnesium oxide nanoparticles can show good bactericidal activity even in the absence of light [2].

Besides being found from magnesium-based minerals, magnesium also can be found in brine water and seawater. With an average magnesium content in seawater of 1300 ppm, the potential of magnesium from seawater is very promising [3]. Bittern is a by-product of the salt processing industry which contains magnesium and potassium salts. From every ton of sea salt produced, there is one cubic meter of bittern as by-product, and every ten cubic meters of bittern contain 1.2 tons of magnesium chloride [4]. Commonly, bittern is discharged back to the sea without further process, whereas bitterns with high salt concentrations will accumulate at the bottom of the sea can endanger ecosystem [5].
In 1943, Robinson et al. patented a precipitation process of magnesium hydroxide from seawater using calcium hydroxide [6]. However, in this process gypsum was formed and become impurities in magnesium oxide product [7], [8]. Another research was conducted by Dong et al. which used ammonia hydroxide to precipitate magnesium hydroxide from desalination plant waste in Singapore which contains 1679 ppm magnesium [9].

Based on research by Jin and Al-Tabbaa, magnesium oxide from bittern has a higher purity and reactivity compared to magnesium oxide from calcined magnesite [10]. Calcination of magnesium hydroxide to produce magnesium oxide has also been studied previously. The higher the calcination temperature, the larger the magnesium oxide size, so that the surface area and its reactivity will decrease [11]–[15].

There are several methods to produce nanoparticles, such as radiation, thermal decomposition, vapor deposition [16]–[18]. However, most of these techniques are relatively expensive and time-consuming. Another simple and cost-effective method is through ultrasonic destruction [19]. The sonochemical process can produce microbubbles in the liquid, followed by the growth and collapse of the bubbles that can raise the surrounding cavity temperatures to more than 5000 K and pressures more than 500 atm. Because bubbles collapse in less than one nanosecond, a cooling rate of more than 1000 K/s can be obtained that can hinder product crystallization. Collapse of the bubbles can also cause shock waves and liquid jets with speeds of more than 400 km/hour. This physical and chemical environment can cause the formation of products with nanoparticle size [20]–[22].

In this research, sodium hydroxide was used to precipitate magnesium ions from bittern. Then, calcination and sonochemical process were performed. We would investigate the effect of sonication time and amplitude as independent variables during sonochemical process to produce magnesium oxide nanoparticles.

2. Materials and Methods

This research was conducted using bittern, sodium hydroxide, and 2-butanol. Bittern was a by-product of salt processing from seawater, while sodium hydroxide and 2-butanol used were PA (pro analysis) materials. Samples characterization was carried out using ICP - OES (Inductively Coupled Plasma - Optical Emission Spectrophotometers), XRD (X-Ray Diffraction), PSA (Particle Size Analyzer), and SEM-EDX (Scanning Electron Microscope-Energy Dispersive X-ray Disorders) Spectroscopy.

The initial stage of this research was to filter 500 ml bittern to remove the solid impurities. Magnesium hydroxide was synthesized by adding sodium hydroxide to the bittern with mol ratio of Mg\(^{2+}\) ion : sodium hydroxide = 1: 2 according to its stoichiometric calculation and then be stirred at 300 rpm and temperature of 30°C. The residue that has been separated from the filtrate then was dried in the oven for 24 hours at 100°C. The solid was calcined at 460°C for 2 hours to produce magnesium oxide. Reduction of magnesium oxide particles from micro-size to nano-size was carried out by ultrasonic method using 2-butanol as sonication media with a ratio of 3 grams magnesium oxide / 200 ml 2-butanol. The amplitude was varied between 20%, 30%, and 40% while sonication time was varied between 4, 8, and 16 minutes.

The concentration of magnesium and other impurities in the bittern and filtrate were analyzed using ICP-OES and were calculated based on mass balance so that magnesium concentration in the residue could be obtained. XRD characterization was used to determine phase composition in the residue before and after calcination. After sonochemical process, the samples were analyzed using the free-settling method. Sample that had the lowest height of supernatant was analyzed using PSA and SEM-EDX to determine the size and morphology of the particles obtained.
3. Result and Discussion

In the previous research by Dong et al., magnesium oxide was synthesized from reject brine from desalination plants in Singapore which contain 1,718 ppm magnesium [9]. While in this research, the bittern was a by-product of salt processing from seawater in Lamongan, East Java, Indonesia. Based on the ICP analysis results that can be seen in Table 1, this bittern has greater magnesium content, which is 76,688.9 ppm.

| Element | B  | Ca | K    | Li  | Mg    | Na    |
|---------|----|----|------|-----|-------|-------|
| Concentration (ppm) | 453.34 | 148.48 | 2,991.1 | 29.05 | 76,688.9 | 3,126.84 |

Magnesium hydroxide was synthesized via the reaction between Mg\(^{2+}\) ions in the brine and OH\(^{-}\) from sodium hydroxide. The possible reactions were as follows:

\[
\text{NaOH (aq)} \leftrightarrow \text{Na}^+ + \text{OH}^- \quad (1)
\]

\[
\text{Mg}^{2+} + 2\text{OH}^- \rightarrow \text{Mg(OH)}_2(s) \quad (2)
\]

The filtrate was separated from solid residue and ICP analysis was carried out to determine concentration of the elements in the filtrate which can be seen in Table 2. Magnesium concentration in the residue and percent of magnesium precipitated could be calculated based on mass balance. Based on these data it can be calculated that the percent of magnesium precipitated was 80%.

| Element | B     | Ca | K    | Li  | Mg    | Na    |
|---------|-------|----|------|-----|-------|-------|
| Concentration (ppm) | 12.23 | 0.87 | 2,807.1 | 0.36 | 15,377.2 | 8,047.62 |

The residue that has been separated from the filtrate then was dried in the oven for 24 hours at 100°C. Figure 1 shows XRD diffractogram of the residue obtained from the reaction between the bittern and sodium hydroxide. From this figure, it can be seen that the main crystalline peak positions are magnesium hydroxide. These peaks are followed by several minor peaks of sodium chloride.

Magnesium hydroxide was calcined at 460°C for 2 hours to produce magnesium oxide. XRD diffractogram of the calcined can be seen in Figure 2. The absence of magnesium hydroxide peak indicates that it was fully decomposed at the calcination process resulting in magnesium oxide. These magnesium oxide peaks are also followed by several minor peaks of sodium chloride.

Reduction of magnesium oxide particles from micro-size to nano-size was carried out by ultrasonic method using 2-butanol as sonication media with a ratio of 3 grams magnesium oxide / 200 ml 2-butanol. The amplitude was varied between 20%, 30%, and 40% while sonication time was varied between 4, 8, and 16 minutes.

The equivalent diameter refers to the size of particles that have irregular shapes. One technique for measuring equivalent diameter is Stokes' diameter which is based on sedimentation process. In sedimentation process, as settling rate approaches zero, clear liquid supernatant zone and settle bed zone are formed. This process is illustrated in the schematic diagram in Figure 3. Based on Stokes’ law that can be seen in Equation 3, factors that affect sedimentation include particles size and shape, solids weight and volume, fluid viscosity, and specific gravity of solids and liquid. At the same specific gravity, particles that have a larger size will have greater terminal velocity [23].
Figure 1. XRD diffractogram of magnesium hydroxide

Figure 2. XRD diffractogram of magnesium oxide
Where:

- \( v \) = Terminal velocity (m s\(^{-1}\))
- \( d \) = Particle diameter (m)
- \( g \) = Gravity acceleration (m s\(^{-2}\))
- \( \rho_s \) = Particle density (kg m\(^{-3}\))
- \( \rho_f \) = Fluid density (kg m\(^{-3}\))
- \( \eta \) = Fluid viscosity (Ns m\(^{-2}\))

After sonication process, each sample was settled for 7 days. Supernatant zone height can be seen in Figure 4. This figure shows that sample with amplitude variation of 30\% and 16 minutes sonication time has the lowest supernatant zone height so that it can be concluded that this sample has the smallest particle diameter. This sample was then analyzed by using PSA.

From Figure 4 we can see that increasing sonication time will decrease the particle size. According to Sáez and Mason, sonication time is one of the parameters that affect particle size during ultrasonic destruction process [24]. Based on Equation 4, dissipated sonic power in liquid is a function of amplitude [25]. However, based on research by Yustanti et al., particles with very small size tend to have agglomeration effect [26]. This causes sample with amplitude variation of 30\% is smaller than samples with amplitude variation of 20\% and 40\%.

From the results of PSA analysis, sample with amplitude variation of 30\% and 16 minutes sonication time has an average particle diameter of 195.7 nanometers that shown in Figure 5. In Figure 6, morphology of the sample can be observed through SEM analysis at 5000x magnification. The particles in this figure have spherical shapes, similar to previous study [27].
Figure 4. Supernatant zone height in various conditions: (a) 4 mins, (b) 8 mins, (c) 16 mins

Where:

\[ P_{\text{diss}} = \frac{1}{2} A^2 (2\pi f)^2 Z \]  \hspace{1cm} (4)

\( P_{\text{diss}} \) = Dissipated sonic power in liquid (W)
A = Amplitude (m)
f = Frequency (Hz)
S = Emitter surface (m\(^2\))
Z = Acoustic impedance (kg m\(^{-2}\) s\(^{-1}\))

Figure 5. Magnesium oxide particle size distribution
4. Conclusion
The results obtained in this present research show that amplitude and sonication time affect the size of the particles produced in the ultrasonic destruction process. Sample with amplitude variation of 30% and 16 minutes sonication time has the smallest particle size, with an average particle diameter of 195.7 nanometers. Increasing sonication time will decrease the particle size. However, particles with very small sizes tend to have an agglomeration effect.

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6. References
[1] S. K. Shukla et al., “Nano-like magnesium oxide films and its significance in optical fiber humidity sensor,” vol. 98, pp. 5–11, 2004.
[2] L. Huang, D. Q. Li, Y. J. Lin, M. Wei, D. G. Evans, and X. Duan, “Controllable preparation of Nano-MgO and investigation of its bactericidal properties,” J. Inorg. Biochem., vol. 99, no. 5, pp. 986–993, 2005.
[3] J. F. Anthoni, “The Chemical Composition of Seawater,” 2006. [Online]. Available: http://www.seafriends.org.nz/oceano/seawater.htm#composition.
[4] A. A. Hussein, K. Zohdy, and M. Abdelkreem, “Seawater Bittern a Precursor for Magnesium Chloride Separation: Discussion and Assessment of Case Studies,” Int. J. Waste Resour., vol. 07, no. 01, pp. 1–6, 2017.
[5] A. M. O. Mohamed, M. Maraqa, and J. Al Handhaly, “Impact of land disposal of reject brine from desalination plants on soil and groundwater,” Desalination, vol. 182, no. 1–3, pp. 411–433, 2005.
[6] H. A. Robinson, R. E. Friedrich, and R. S. Spencer, “MAGNESUM HYDROXDE FROM SEAWATER,” US 2405055, 1943.
[7] J. W. An, D. J. Kang, K. T. Tran, M. J. Kim, T. Lim, and T. Tran, “Recovery of lithium from Uyuni salar brine,” Hydrometallurgy, vol. 117–118, pp. 64–70, 2012.
[8] T. Karidakis, S. Agatzini-Leonardou, and P. Neou-Syngouna, “Removal of magnesium from nickel laterite leach liquors by chemical precipitation using calcium hydroxide and the potential use of the precipitate as a filler material,” Hydrometallurgy, vol. 76, no. 1–2, pp. 105–114, 2005.
[9] H. Dong, C. Unluer, E. H. Yang, and A. Al-Tabbaa, “Synthesis of reactive MgO from reject brine via the addition of NH4OH,” *Hydrometallurgy*, vol. 169, pp. 165–172, 2017.

[10] F. Jin and A. Al-Tabbaa, “Characterisation of different commercial reactive magnesia,” *Adv. Cem. Res.*, vol. 26, no. 2, pp. 101–113, 2014.

[11] L. Mo, M. Deng, and M. Tang, “Effects of calcination condition on expansion property of MgO-type expansive agent used in cement-based materials,” *Cem. Concrr. Res.*, vol. 40, no. 3, pp. 437–446, 2010.

[12] E. Alvarado, L. M. Torres-Martinez, A. F. Fuentes, and P. Quintana, “Preparation and characterization of MgO powders obtained from different magnesium salts and the mineral dolomite,” *Polyhedron*, vol. 19, no. 22–23, pp. 2345–2351, 2000.

[13] J. K. Bartley, C. Xu, R. Lloyd, D. I. Enache, D. W. Knight, and G. J. Hutchings, “Simple method to synthesize high surface area magnesium oxide and its use as a heterogeneous base catalyst,” *Appl. Catal. B Environ.*, vol. 128, pp. 31–38, 2012.

[14] W. R. Eubank, “Calcination Studies of Magnesium Oxides,” *J. Am. Ceram. Soc.*, vol. 34, no. 8, pp. 225–229, 1951.

[15] K. Itatani, K. Koizumi, F. S. Howell, A. Kishioka, and M. Kinoshita, “Agglomeration of magnesium oxide particles formed by the decomposition of magnesium hydroxide - Part 2 Agglomeration at fixed temperatures,” *J. Mater. Sci.*, vol. 24, no. 7, pp. 2603–2609, 1989.

[16] Y. H. Kim, D. K. Lee, B. G. Jo, J. H. Jeong, and Y. S. Kang, “Synthesis of oleate capped Cu nanoparticles by thermal decomposition,” *Colloids Surfaces A Physicochem. Eng. Asp.*, vol. 284–285, pp. 364–368, 2006.

[17] A. A. Ponce and K. J. Klabunde, “Chemical and catalytic activity of copper nanoparticles prepared via metal vapor synthesis,” *J. Mol. Catal. A Chem.*, vol. 225, no. 1, pp. 1–6, 2005.

[18] C. Yeh, “Formation and Characteristics of Cu Colloids from CuO Powder by Laser Irradiation in,” pp. 6851–6857, 2000.

[19] V. Zin, B. G. Pollet, and M. Dabalá, “Sonoelectrochemical (20 kHz) production of platinum nanoparticles from aqueous solutions,” *Electrochim. Acta*, vol. 54, no. 28, pp. 7201–7206, 2009.

[20] S. J. Doicrycz and K. S. Suslick, “Interparticle Collisions Driven by Ultrasound,” vol. 2, no. 67, pp. 1987–1989, 1987.

[21] K. S. Suslick, “The Chemical Effects of Ultrasound,” *Sci. Am.*, pp. 80–86.

[22] A. Gedanken, “Using sonochemistry for the fabrication of nanomaterials,” vol. 11, pp. 47–55, 2004.

[23] B. A. Wills, J. A. Finch, B. A. Wills, and J. A. Finch, “Chapter 4 – Particle Size Analysis,” *Wills’ Miner. Process. Technol.*, pp. 91–107, 2016.

[24] V. Sáez and T. J. Mason, “Sonoelectrochemical synthesis of nanoparticles,” *Molecules*, vol. 14, no. 10, pp. 4284–4299, 2009.

[25] Ratoarinoro, F. Contamine, A. M. Wilhelm, J. Berlan, and H. Delmas, “Power measurement in sonochemistry,” *Ultrason. Sonochem.*, vol. 2, no. 1, pp. 43–47, 1995.

[26] E. Yustanti, M. A. E. Hafizah, and A. Manaf, “Synthesis of strontium substituted barium titanate nanoparticles by mechanical alloying and high power ultrasonication destruction,” *AIP Conf. Proc.*, vol. 1725, no. 2016, pp. 0–6, 2016.

[27] M. A. Alavi and A. Morsali, “Syntheses and characterization of Mg(OH)2 and MgO nanostructures by ultrasonic method,” *Ultrason. Sonochem.*, vol. 17, no. 2, pp. 441–446, 2010.