

Magnesium oxide (MgO) nanoparticles have been widely used in a variety of applications because of their good surface reactivity. Magnesium oxide from bittern has a larger surface area compared to magnesium oxide from calcined magnesite and magnesium ions precipitation from bittern using sodium hydroxide has higher purity than using calcium hydroxide or ammonium hydroxide. In this research, sodium hydroxide was added to a bittern solution obtaining magnesium hydroxide precipitate, followed by the calcination process to produce magnesium oxide. Nano magnesium oxide was synthesized by the ultrasonic destruction process using ethanol and 2-propanol as media. In this study, sonication time and particle concentration effect on the ultrasonic destruction process were investigated. During the process, the sonication time was varied between 8, 16, 32, 64, and 128 minutes while the magnesium oxide concentration was varied between 1 %, 2 %, and 3 %. Increasing sonication time and particle concentration will decrease the particle size. The previous study shows that particles with very small sizes tend to have an agglomeration effect. The aim of this work is to optimize nano magnesium oxide production from bittern. Surfactant addition was also studied to prevent agglomeration between particles. Four types of surfactant namely anionic (sodium lauryl sulfate), cationic (cetyl tri-methyl-ammonium bromide), amphoteric (fatty acid amido alkyl betaine), and non-ionic (nonylphenol 10 ethoxylated) with a concentration of 1 % and a volume of 0.125 ml were added during the second ultrasonic destruction process. All types of surfactants have a positive effect to prevent agglomeration during the ultrasonic destruction process, with the amphoteric surfactant having the highest performance

Keywords: *magnesium oxide, nanoparticles, bittern, ultrasonic destruction, surfactants, anionic, cationic, amphoteric, non-ionic*

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INVESTIGATION OF SURFACTANT EFFECT DURING SYNTHESIS OF MAGNESIUM OXIDE NANOPARTICLES FROM BITTERN USING ULTRASONIC DESTRUCTION PROCESS

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1. Introduction

Nanoparticles are receiving significant attention due to their excellent properties, which are different from their microparticles. Their high optical, chemical, thermal, electrical properties are due to the large surface-to-volume ratio [1]. While magnesium oxide is mostly used in refractory, fertiliz-

er, and other chemical industries; magnesium oxide nanoparticles can be used as sensors [2], bactericide [3], catalyst in the ozonation process [4], high-temperature superconductor thick films [5], tumor treatment [6].

Magnesium oxide from bittern has a larger surface area and higher purity compared to magnesium oxide from calcined magnesite [7]. Bittern is a salt processing by-product,

which still contains 0.1 tonnes of magnesium chloride per cubic meter [8]. Currently, bittern is discharged back to the sea without further processing. High salt concentrations in bittern can cause water pollution and endanger the ecosystem [9]. On the other hand, bittern contains valuable materials, which can be extracted and processed to become high-value products even though it is still challenging.

2. Literature review and problem statement

Magnesium ions precipitation from bittern using sodium hydroxide has higher purity than using calcium hydroxide or ammonium hydroxide [10]. Previous experiments show that magnesium hydroxide was synthesized with 95.4% and 93.5% purity using sodium hydroxide and ammonium hydroxide, respectively [11]. Gypsum becomes the main impurity when magnesium ion was precipitated using calcium hydroxide [12].

Ultrasonic destruction is widely used to produce nanoparticles because of being a green, simple, and cost-effective process [13]. Other methods, namely radiation [14], thermal decomposition [15], and vapor deposition [16] are more expensive and time-consuming. During the ultrasonic destruction process, microbubbles form, grow, and then collapse, which increase surrounding cavity temperature to more than 5,000 K and pressure to more than 500 atm [17]. The collapse of the microbubbles also causes shock waves and 400 km/hour liquid jets [18]. This chemical and physical environment can cause the formation of nanoparticles product.

Based on previous research, particles with very small sizes produced by the ultrasonic destruction method tend to have an agglomeration effect [19]. In order to overcome this problem, surfactant was added during the ultrasonic destruction process. Surfactants have the ability to reduce the surface tension of a medium and reduce the interfacial tension between two phases with different degrees of polarity, and wetting agent characteristics also help prevent agglomeration [20]. Surfactants are molecules that consist of a non-polar hydrophobic part and polar hydrophilic part. The hydrophobic part usually is a hydrocarbon, while the hydrophilic part can be ionic, non-ionic, or amphoteric. Anionic surfactants contain a negative charge, cationic surfactants contain a positive charge, while amphoteric surfactants contain both anionic and cationic groups.

Several studies have been conducted to synthesize nanoparticles with surfactant addition. Polyvinylpyrrolidone (non-ionic surfactant) was added during silver nanoparticle synthesis [21]. The properties of titanium dioxide under the influence of sodium dodecyl sulfate (anionic surfactant) were investigated [22]. Agglomeration behavior of two different cationic surfactants was studied during the synthesis of zinc oxide nanoparticles [23]. Therefore, in this research, different types of sur-

factants (anionic, cationic, amphoteric, and non-ionic) were added to investigate their effect to hinder agglomeration during synthesis of magnesium oxide nanoparticles.

3. The aim and objectives of the study

The aim of this study is to investigate the effect of surfactant addition during the ultrasonic destruction process to synthesize magnesium oxide nanoparticles.

To achieve this aim, the following objectives are accomplished:

- to study the effect of sonication time, media, and particle concentration during the ultrasonic destruction process;
- to observe the effect of surfactant addition during the ultrasonic destruction process by measuring magnesium oxide particle size.

4. Materials and method

This research was conducted using bittern, sodium hydroxide, ethanol, 2-propanol, sodium lauryl sulfate (anionic surfactant), cetyl tri-methyl-ammonium bromide (cationic surfactant), fatty acid amido alkyl betaine (amphoteric surfactant), and nonylphenol 10 ethoxylated (non-ionic surfactant). Bittern used was from Lamongan, East Java, Indonesia, while other materials were PA (pro analysis) materials. Samples characterizations were carried out using XRD (X-Ray Diffraction), ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrophotometers), SEM-EDX (Scanning Electron Microscope-Energy Dispersive X-ray Disorders Spectroscopy), and PSA (Particle Size Analyzer). In this research, the free-settling method illustrated in the schematic diagram in Fig. 1 was used to help measure particle diameter. After the ultrasonic destruction process, each sample was settled for 7 days. Larger particles with the same specific gravity will take less time to settle, resulting in a greater height of the supernatant zone.

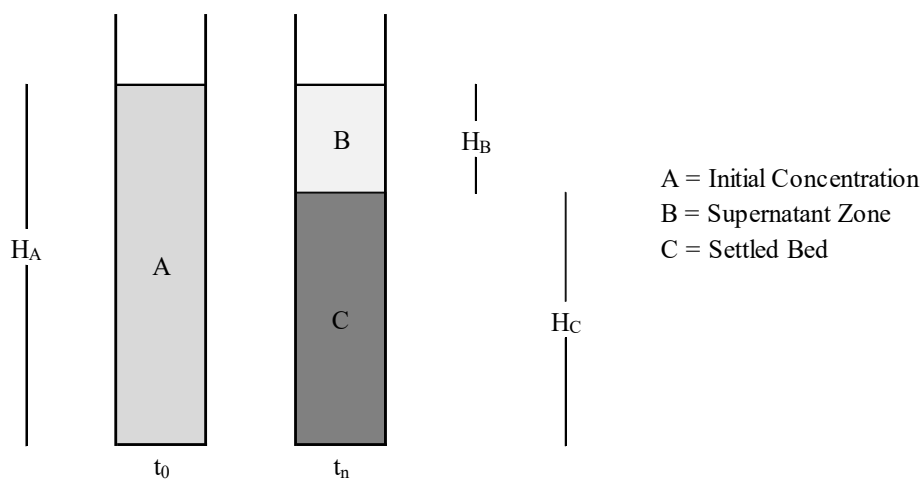


Fig. 1. Batch settling process

Sodium hydroxide was added to bittern with a mole ratio of Mg^{2+} ion: sodium hydroxide=1:2 and then stirred at 300 rpm and room temperature for 6 hours to obtain magnesium hydroxide. Magnesium concentrations in the

bittern and filtrate were analyzed using ICP-OES so that the percent of magnesium precipitated could be calculated. The residue was dried in the oven at 100 °C for 24 hours and then calcined for 2 hours at 460 °C to synthesize magnesium oxide. XRD characterization was used for phase identification of residue before and after calcination. The ultrasonic destruction process was carried out to reduce magnesium oxide particles from micro to nanoscale particles using ethanol and 2-propanol as media. The amplitude was 30 %, while the time was varied between 8, 16, 32, 64, and 128 minutes. Variations in the magnesium oxide concentration were also carried out between 1 %, 2 %, and 3 %. Surfactant with 1 % concentration and 0.125 ml volume was added to 50 ml of the solution from the previous ultrasonic destruction to do the second ultrasonic destruction process for 15 minutes. The sample that had the lowest height of the supernatant zone of the free-settling method was analyzed using SEM-EDX and PSA to determine the morphology and size of the particles obtained.

supernatant zone height than the sample at 64 minutes sonication time.

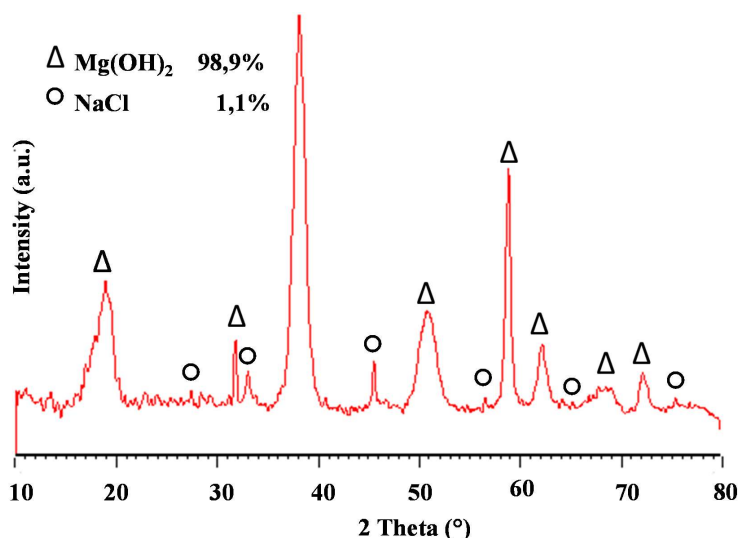


Fig. 2. XRD pattern of magnesium hydroxide

5. Experimental results of synthesizing nano magnesium oxide from bittern using the ultrasonic destruction process

5. 1. Effect of the sonication time, media, and particle concentration during the ultrasonic destruction process

The chemical composition of the brine and filtrate obtained via ICP-OES analysis is summarized in Table 1. The precipitation rate of magnesium after the reaction of brine with sodium hydroxide was 80 %. Fig. 2, 3 show XRD patterns of the residue obtained from the precipitation and calcination process, respectively.

The diffraction patterns of the residue from the precipitation process in Fig. 2 demonstrated the presence of magnesium hydroxide along with several minor peaks of sodium chloride. The main peaks of magnesium oxide in Fig. 3 replacing magnesium hydroxide peaks in Fig. 2 show that the residue was fully decomposed during the calcination process. These magnesium oxide peaks are accompanied by a few minor peaks of sodium chloride.

In this research, ethanol and 2-propanol are used as media in the ultrasonic destruction process. The supernatant zone height was measured and shown in Fig. 4.

It can be seen from Fig. 4 that the sample using ethanol as a medium has a lower supernatant zone height than the sample using 2-propanol. Longer sonication time will decrease the supernatant zone height. However, the sample using 2-propanol as a medium at 128 minutes sonication time has a lower

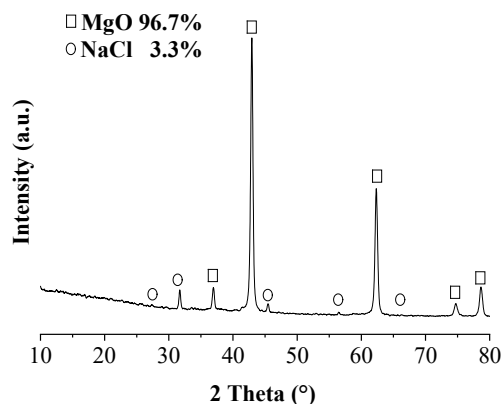


Fig. 3. XRD pattern of magnesium oxide

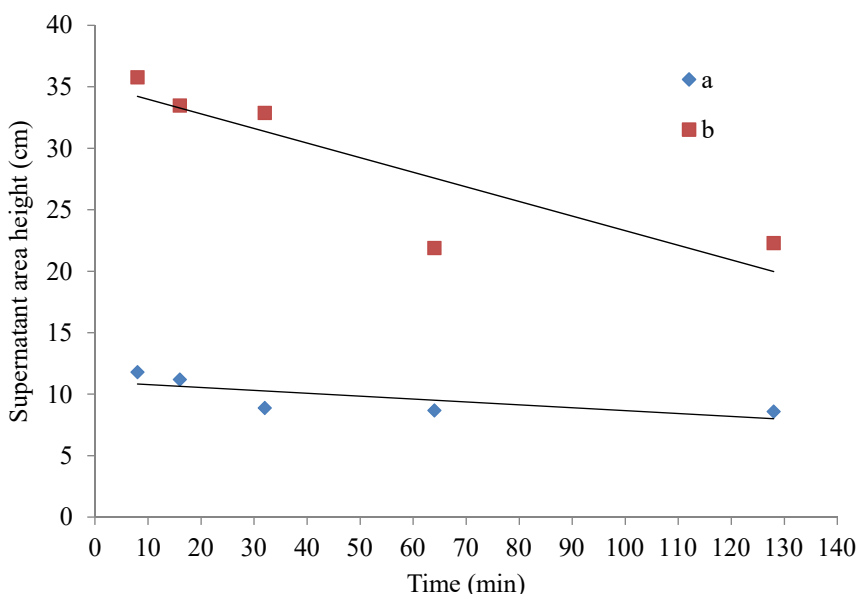


Fig. 4. Supernatant zone height in various times using media: a – Ethanol; b – 2-Propanol

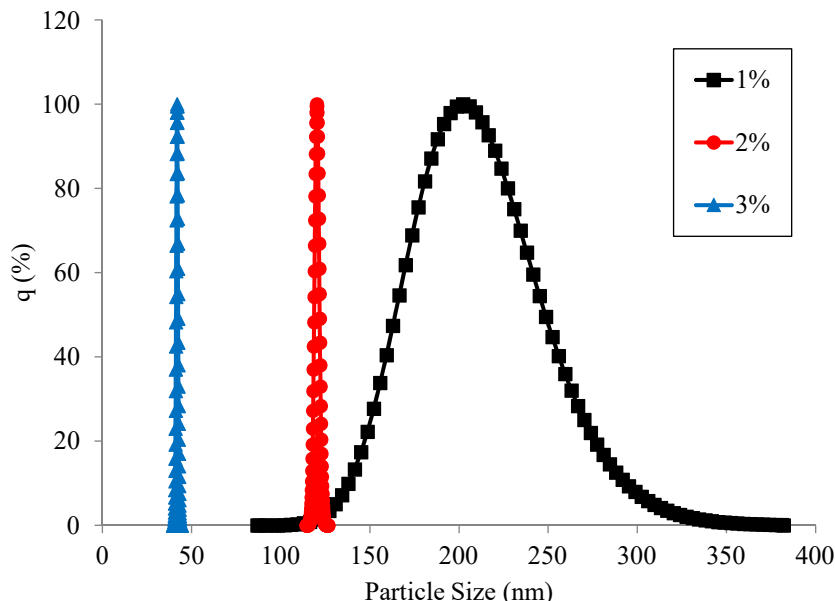


Fig. 5. Particle size distribution in various magnesium oxide concentrations

MgO concentrations were varied between 1 %, 2 % and 3 % using ethanol as a medium for 128 minutes. Fig. 5 shows PSA analysis that measures the average particle size of the magnesium oxide products.

diameter, 2 % MgO concentration results in 120 nm average particle diameter, and 3 % MgO concentration results in 42 nm average particle diameter.

Table 1

Chemical composition of the brine and filtrate

Element	B	Ca	K	Mg	Na
Brine Concentration (ppm)	453.34	148.48	2,991.1	76,688.9	3,126.84
Filtrate Concentration (ppm)	12.23	0.87	2,807.1	15,377.2	8,047.62

Increasing concentration will decrease the particle size, as 1 % MgO concentration results in 211 nm average particle

5. 2. Effect of surfactant addition during the ultrasonic destruction process

From Fig. 6 we can see that all samples with surfactant addition show a lower supernatant zone height compared to the sample without surfactant addition, and the sample with the addition of amphoteric surfactant has the lowest height of the supernatant zone.

Fig. 7 shows PSA analysis that measures the average particle size of the magnesium oxide products with and without the addition of amphoteric surfactant, while Fig. 8 shows SEM images of the magnesium oxide products with and without the addition of amphoteric surfactant.

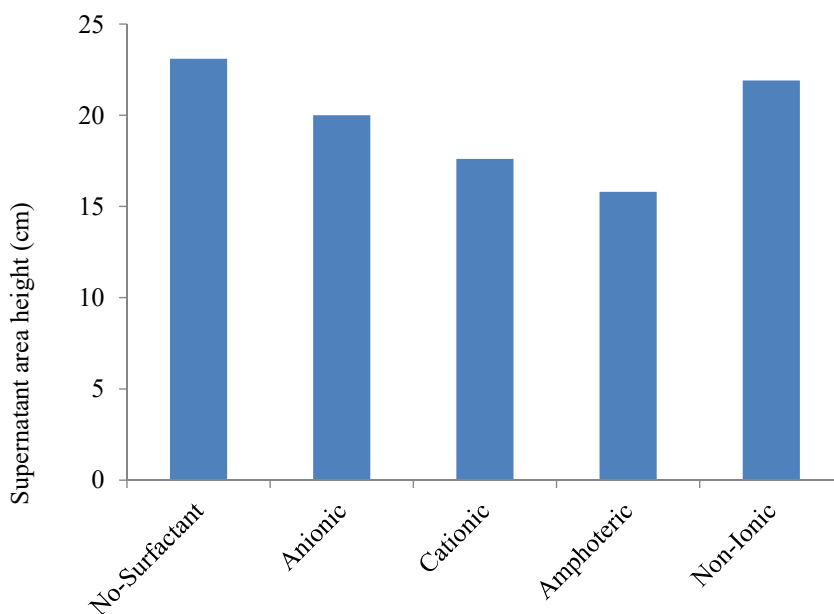


Fig. 6. Supernatant zone height using various surfactants

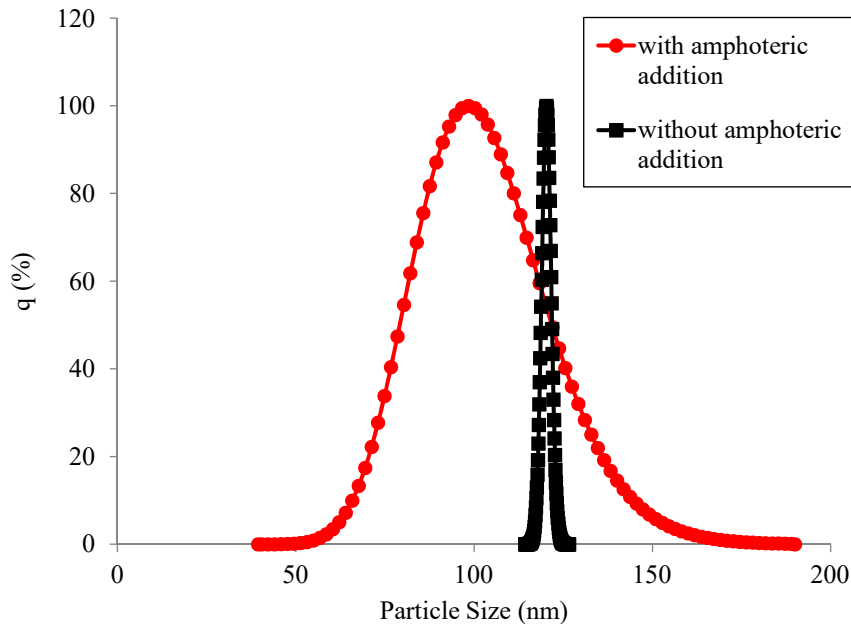
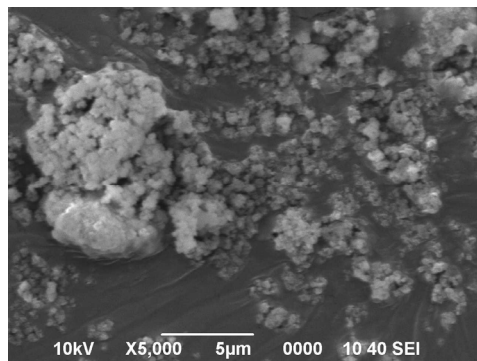
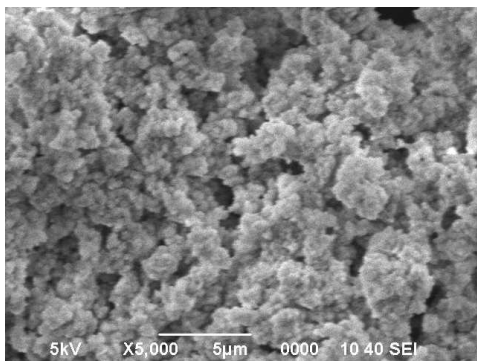


Fig. 7. Particle size distribution with and without the addition of amphoteric surfactant



a



b

Fig. 8. SEM images of magnesium oxide: *a* – with the addition of amphoteric surfactant; *b* – without the addition of amphoteric surfactant

The average particle size of the magnesium oxide products is 102.9 and 120.3 nanometers for the samples with and without surfactant addition, respectively. Particle morphology through SEM analysis at 5000x magnification shows spherical magnesium oxide particles for both samples, with or without the addition of amphoteric surfactant.

6. Discussion of experimental results of synthesizing nano magnesium oxide from bittern using the ultrasonic destruction process

Smaller particles with the same specific gravity will result in a lower height of the supernatant zone. Fig. 4 shows that longer sonication time decreases the supernatant zone height, which indicates the decrease of the particle size. The sonochemical process induces erosion formed by fatigue, so a longer sonication time will decrease the particle size [24]. However, after 64 minutes the decrease in particle size was not significant.

Agglomeration effect can be seen as the sample using 2-propanol at 64 minutes sonication time has a smaller particle size than the sample at 128 minutes sonication time. This phenomenon was caused by Van der Waals force that initiates the formation of agglomerates between fine particles [25]. Increasing concentration

will decrease particle size, by the reason of more particles collided with each other so that the particles are reduced to a smaller size.

Both ethanol and 2-propanol used as media in the ultrasonic destruction process are alcohol. Due to the non-polar nature of alcohol while magnesium oxide is polar, magnesium oxide cannot dissolve in alcohol so it will be easier in the separation process. Ethanol and 2-propanol have a similar density, respectively 0.790 and 0.786 g/cm³, whereas their viscosities are 1,074 and 2,038 mPa·s, respectively.

The difference in the viscosity of the media shows that it has an effect on the ultrasonic destruction process, because increasing viscosity will increase the bubble lifetime but decrease the maximum bubble radius and the stress produced by cavitation bubbles [26].

Each type of surfactant has different ways to stabilize particles and prevent agglomeration. Non-ionic surfactants utilize steric effect as stabilization. Steric stabilization is achieved by adsorption of polymer to the surface, forming a thin layer, which prevents Van der Waals force that causes agglomeration. Ionic surfactants use an electrostatic stabilization mechanism, which occurs due to the addition of charge into colloidal particles so that repulsion occurs between particles [27]. From these experiments, the addition of amphoteric surfactant shows the highest performance to prevent agglomeration during the ultrasonic destruction process.

The average particle size of the products is 102.9 and 120.3 nanometers for the samples with the addition of amphoteric surfactant and without surfactant addition, respectively. Even though with the addition of amphoteric surfactant the decrease of the average particle size is insignificant and the average particle size is still more than 100 nanometers, half of the particles have a size distribution below 100 nanometers while without surfactant addition all the particles have a size distribution above 100 nanometers. However, this research can be used as basic reference for further development of synthesizing magnesium oxide

nanoparticles from bittern. Variations of surfactant volume and concentration are needed to determine optimum surfactant addition during the ultrasonic destruction process to reduce the agglomeration effect since magnesium oxide nanoparticles synthesized in this study still have an average particle size of more than 100 nanometers.

7. Conclusions

1. An increase in sonication time and particle concentration during the ultrasonic destruction process reduced particle size, while a decrease in viscosity will decrease the particle size of magnesium oxide. Using ethanol as a medium and 3% magnesium oxide concentration for 128 minutes during the ultrasonic destruction process resulted in an average diameter of magnesium oxide of 41.88 nanometers.

2. The addition of anionic, cationic, amphoteric, and non-ionic surfactants during the ultrasonic destruction process shows a positive effect in preventing agglomeration. Amphoteric surfactant shows the highest performance. The addition of fatty acid amido alkyl betaine (amphoteric surfactant) resulted in the smallest particle size of magnesium oxide with an average diameter of 102.9 nanometers.

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