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Preparation of nano-magnesium oxide from Indonesia local seawater bittern using the electrochemical method

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ABSTRACT

In this study, nano-size MgO was synthesized from seawater and bittern obtained from local salt industry in Pamekasan, Madura, Indonesia, using electrochemical method. The main purpose was to study the effects of seawater pre-concentration and bittern dilution on the structure and morphology of the MgO nanoparticles produced. Electrochemical process was performed in a two-compartment electrochemical cell with a fixed potential of 18 V, for 4 h at ambient temperature, and without adjusting the pH. Solid $Mg(OH)_2$ produced was converted into MgO by calcination treatment at 500 C for 4 h, and then characterized using XRD and SEM technique. The characterization results revealed that spherical or cubic crystalline MgO were successfully produced, with the particle sizes in the range of 60–100 nm.

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Introduction

Preparation of magnesium hydroxide, $Mg(OH)_2$ from magnesium chloride, $MgCl_2$, produced from seawater or bittern as reported in previous study[1] is an attractive method since $Mg(OH)_2$ is one of the essential precursors of MgO.[2] Both $Mg(OH)_2$ and MgO are important applied materials widely used in various fields such as pharmaceutical ingredients,[3–5] resin additives,[6,7] paper preservatives,[8] catalyst support,[9,10] and electro-optical devices.[11]

Production of $Mg(OH)_2$ is generally carried out by precipitation method, in which alkaline reagents such as ammonium hydroxide (NH_4OH) [12] and sodium hydroxide (NaOH)[13,14] is added into Mg^{2+} solution. In this method, Mg^{2+} is converted to $Mg(OH)_2$, which is insoluble in water, according to the Equation 1.

$$Mg^{2+}_{(aq)} + 2OH^-_{(aq)} \rightarrow Mg(OH)_{2(s)} \quad (1)$$

The basic principle of $Mg(OH)_2$ precipitation is the increase of the pH of the solution into alkaline level, to provide OH in sufficient concentration to react with Mg^{2+} present. The alkalinity of seawater or bittern can be increased electrochemically as indicated in redox reactions presented in Equation 2 and Equation 3.

Cathode:

$$2H_2O_{(l)} + 2e \rightarrow H_{2(g)} + 2OH_{(aq)} \quad (2)$$

Anode:

$$2Cl_{(aq)} \rightarrow Cl_{2(g)} + 2e \quad (3)$$

The OH^- ions formed at the cathode as a result of water reduction will then react with Mg^{2+} ions to produce $Mg(OH)_2$ as shown in Equation 1.

In an attempt to explore the potential of electrochemical method, in our previous study,[15] this method was employed to recover Mg^{2+} from bittern, with the main objective to evaluate the effect of dilution, potential, and electrolysis time on the percent of recovery and purity of $Mg(OH)_2$ obtained. The electrochemical process was carried out using two-compartment electrochemical cells, connected by a salt bridge made of NaCl suspended in gelatin, nickel as a cathode and carbon as an anode. The results show that percent recovery and purity of $Mg(OH)_2$ are influenced by the factors investigated. The best result was obtained from diluted bittern with dilution factor of 4, potential of 18 Volt, and electrolysis time of 4 h. Under these experimental conditions, as much as 85% of Mg^{2+} was successfully converted into $Mg(OH)_2$ with the purity of 91%. In this regard, the present study is a continuation of the aforementioned

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previous study, extending the investigation by including seawater and production of nano-size MgO.

Experimental

Seawater and bittern were obtained from Pamekasan, Madura, Indonesia. The concentration of Mg^{2+}, together with other main cations, in seawater and bittern were analyzed, using inductively coupled plasma-optical emission spectroscopy (715 ES, Variants), and the results are shown in Table 1. As can be seen, the content of Mg^{2+} ions in seawater is 3.29 g/L (0.137 mol/L) and bittern is 53.46 g/L (2.23 mol/L). Prior to electrochemical experiments, the seawater was boiled to adjust the concentration of Mg^{2+} in the range of 0.137–0.219 mol/L. For bittern, the sample was diluted with distilled water to adjust the concentration of Mg^{2+} in the range of 0.278–2.23 mol/L using distilled water.

Table 1. Composition of primary elements in seawater and bittern.

Ions (g/L)	Na^{+}	K^{+}	Mg^{2+}	Ca^{2+}
Seawater	15.85	0.46	1.76	0.55
Bittern	17.31	57.57	53.37	30.15

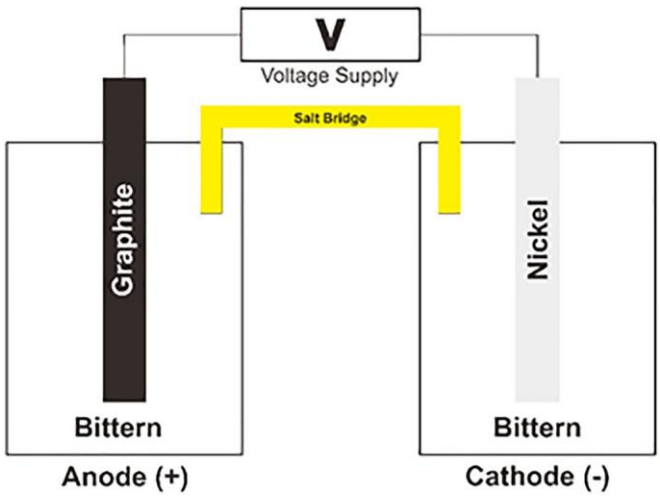

Figure 1. The electrochemical set-up used in this study.

The electrochemical process was performed using a 2-compartment cell connected by a salt bridge, as illustrated in Figure 1. The experiment was carried out at a potential of 18 Volt, for 4 h, at ambient temperature and without adjusting the pH of the sample. The selection of experimental conditions was based on the results of previous study presented in Figures 2 and 3.[15] The product obtained was filtered with a vacuum filter and then washed three times with distilled water to remove any remaining impurities. The sample was dried at 110 C and then calcined at 500 C for 4 h in a muffle furnace to produce MgO powder. The final product analyses were carried out using X-ray fluorescence (Epsilon 3, PANAnalytical), morphology and particle size using SEM (FEI Inspect-S50) and identification of the phases using XRD (Pro expert, PANAnalytical) with Cu Ka radiation (k ¼ 1.5406 Å). The acceleration and current voltages used were 40 kV and 30 mA, respectively. Difractogram recorded in the range of 10–80 in continuous scan mode, with scanning speed of 2 (deg/min).

Results and discussion

Figure 4 shows the effect of concentrated seawater on the levels of MgO produced. After the electrochemical process, $Mg(OH)_2$ was converted to MgO particles by calcination at 500 C for 4 h. This treatment was taken based the study by Park et al.,[16] who reported that $Mg(OH)_2$ was converted to MgO nanoparticles with heat treatment at 500 C for 4 h.

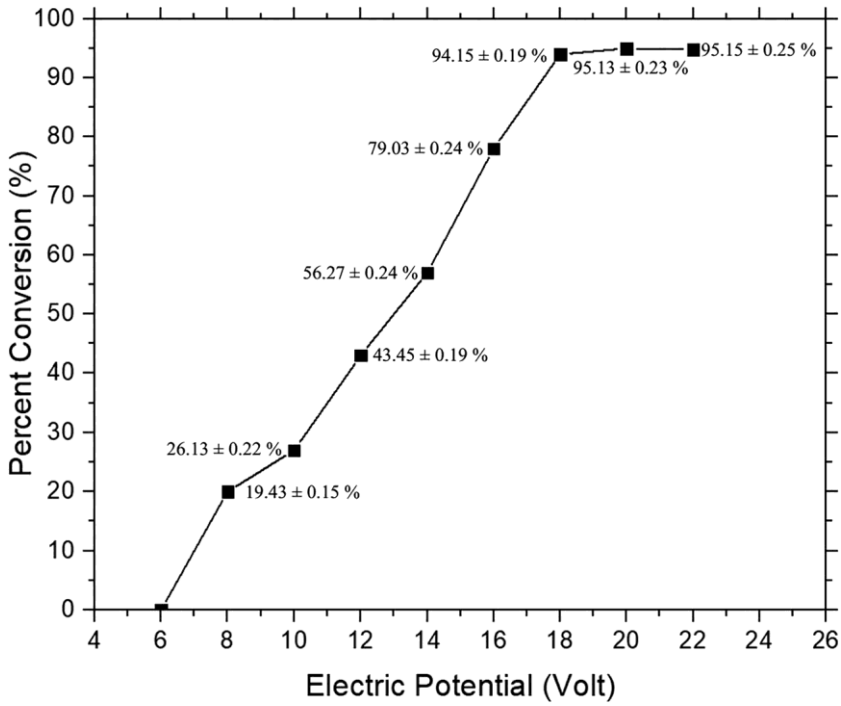

Figure 2. Effect of electric potential on the percent conversion of $Mg(OH)_2$ obtained from bittern.

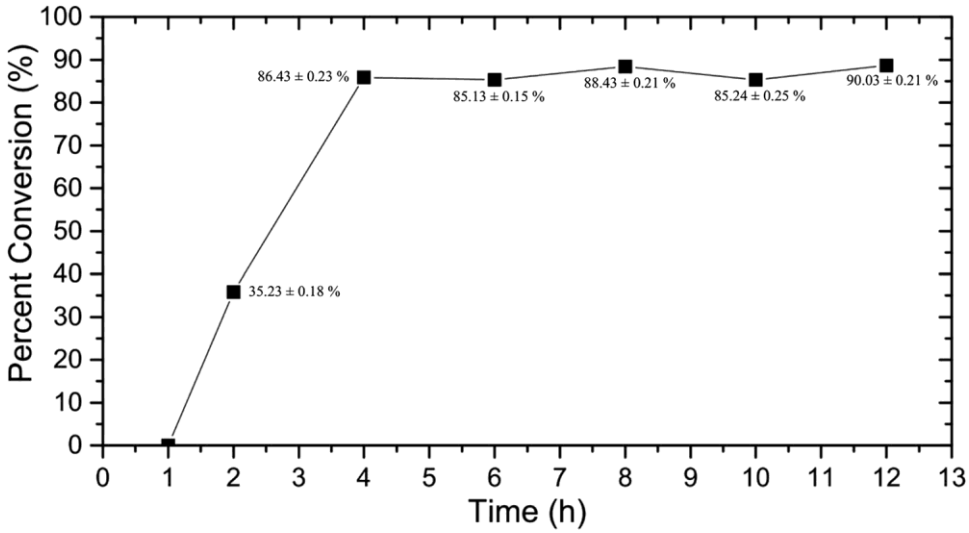

Figure 3. Effect of electrolysis times on the percent conversion of $Mg(OH)_2$ obtained from bittern.

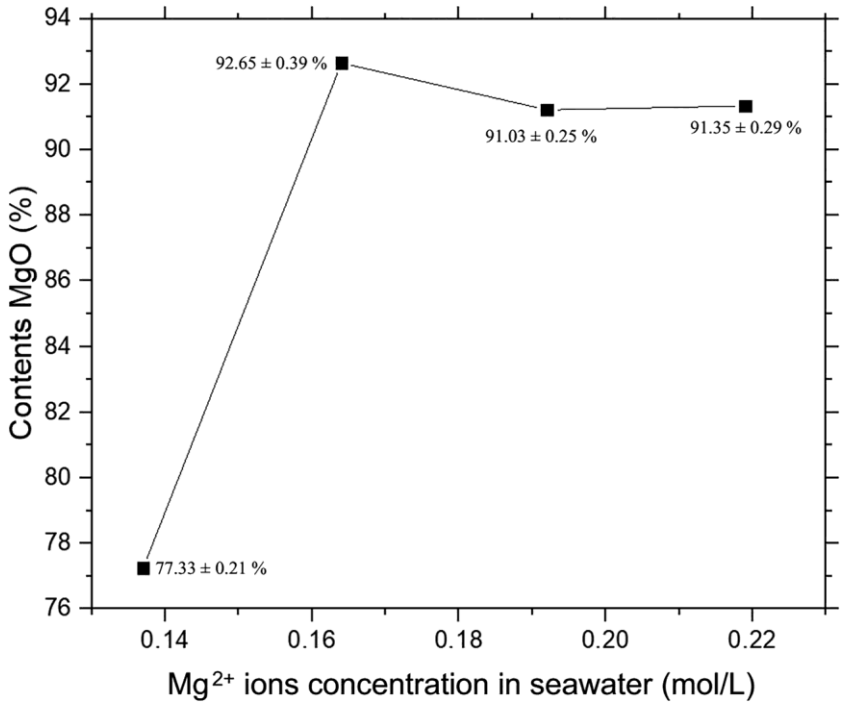

Figure 4. Effect of reconcentration seawater on the contents of MgO.

From seawater samples, the MgO with the highest purity (92.65%.) was obtained from seawater with concentration of Mg^{2+} concentration of 0.16 mol/L, suggesting that, to some extent, the concentrations of Mg^{2+} in the samples influence the purity of MgO produced. Jiang et al.[17] explained that in the electrolysis of seawater, the concentration of ions contained in seawater affects the rate of formation of hydrogen gas and hydroxide ions. In work by Alamdari et al.[13] it was explained that in the process of precipitation of Mg^{2+} ions to $Mg(OH)_2$, the concentration of ions in seawater and the rate of alkali addition influence the nucleation process and the rate of crystal growth that affected the purity of the $Mg(OH)_2$ crystals produced.

Figure 5 shows the effect of dilution of bittern on the purity of MgO produced, showing that dilution led to increased purity of the product. The best result (the purity of 91.21%.) was obtained by diluting the bittern four times (0.557 mol/L ion Mg^{2+}). Figure 6 shows SEM micrograph of MgO produced from seawater with Mg^{2+} concentration of 0.16 mol/L and diluted bittern with Mg^{2+} concentration of 0.557 mol/L. The micrographs display quite similar morphologies, characterized by the existence of globular and cubic shapes with round edges particles. It is interesting to note that the particle size in the nanoscale could be inferred from the micrographs, in which a globular structure formed by aggregate of particles having a diameter around 100 nm.

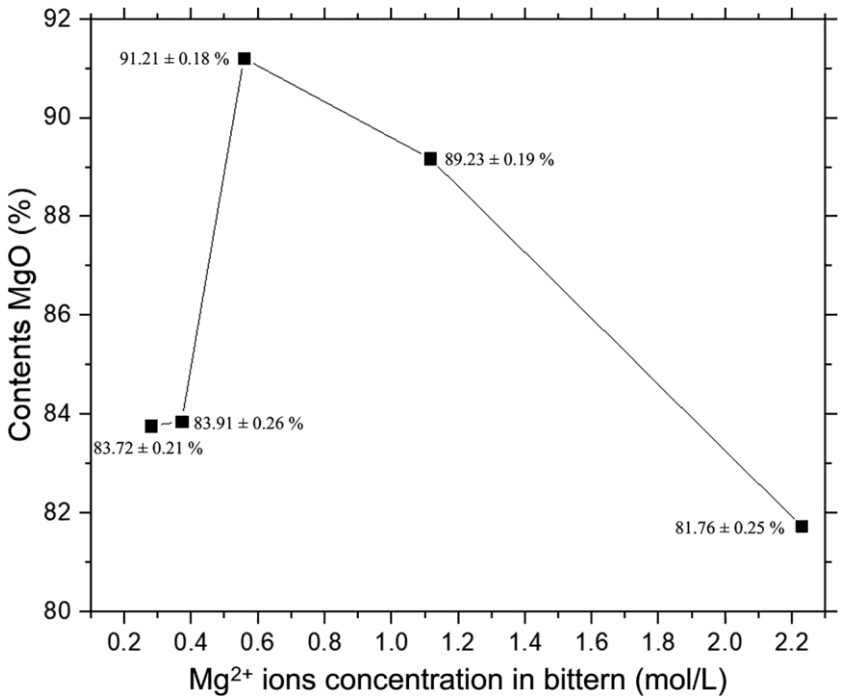

Figure 5. Effect of dilution bittern on the contents of MgO.

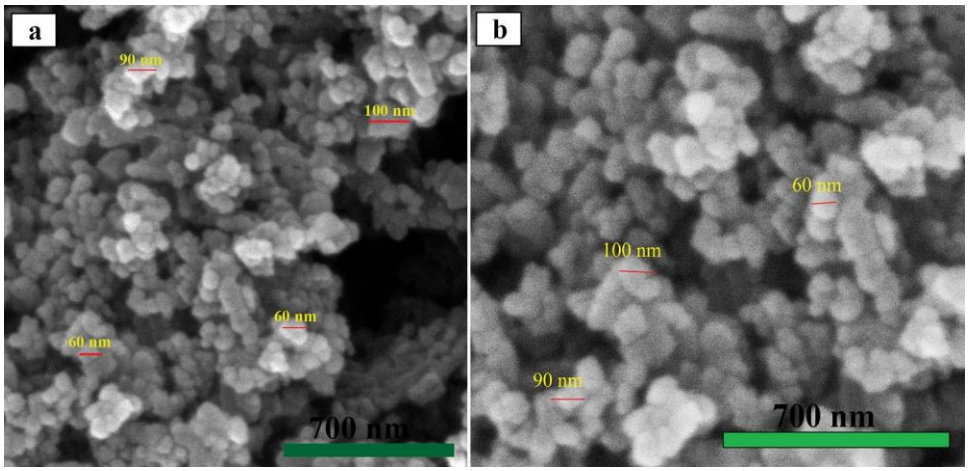

Figure 6. SEM micrographs of synthesized MgO samples: (a) seawater; (b) bittern.

Amrulloh et al.[15] reported that the structure of $Mg(OH)_2$, based on the SEM images obtained showed similarity to the hexagonal platelet structure with a thickness of 60–100 nm.

Figure 7 shows the X-ray diffraction (XRD) pattern of the standard and the resulting products. Samples were obtained from pre-concentrated seawater with Mg^{2+} con- centration of 0.16 mol/L and diluted bittern with the Mg^{2+} concentration of 0.557 mol/L. The XRD pattern of MgO sample produced from seawater indicates the existence of peaks at diffraction angle (2Θ) of 17.9, 31.5, 42.7, 45.2,
50.6, 58.6, 62.1, 75.1, and 78.4 . The peaks at 2Θ of 42.7 and 62.1 are characteristic peaks of crystalline MgO structure, while the rest of the peaks are associated with NaCl. Practically similar pattern was observed in the diffractogram of the sample produced from bittern. Both diffractograms suggest the existence of nano-MgO prepared as a cubic crystal (JCPDS 89-7746).

Table 2 gives the chemical composition of the samples produced determined using XRF analysis. XRF analysis showed that MgO produced from seawater has the purity of 92.65%, and that produced from bittern has the purity of 91.21%. Park et al. [16] synthesize nano MgO from bittern using decarboxylation and deposition methods. In the study, bittern was diluted 5–10 times and then precipitated by adding NaOH and $Ca(OH)_2$ solution followed by decarb- oxylation using a sulfuric acid solution. The MgO produced was reported to have the purity of 99.5%, with particle size of 50–180 nm, globular cubes.

It should be acknowledged that the MgO produced from seawater and bittern still contains NaCl as impurity. Several purification methods have been reported, which in general can be distinguished into pretreatment of raw materials and post-synthesis purification. In the pretreatment method, decarboxylation process was done by adding sulfuric acid

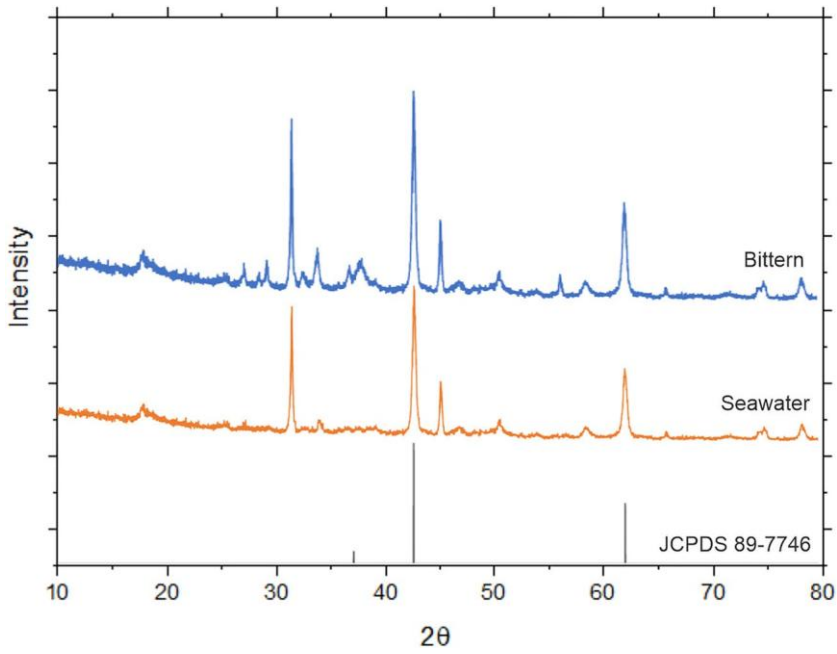

Figure 7. XRD patterns of samples related to MgO.

Table 2. Composition of the main element in MgO samples.

Contents	Seawater	Bittern
MgO	92.65	91.21
SiO_2	2.26	0.98
Cl	1.14	2.21
Other	3.95	5.60

solution after the electrolysis process to remove impurities during the nucleation process and the growth of $Mg(OH)_2$ crystals.[16] In the post-synthesis method, the MgO produced was washed with distilled water to discharge water soluble NaCl impurity, increasing the purity of insoluble MgO as a result.[18]

Conclusions

This study has demonstrated the potential of electrochemical for production of nano-size crystalline MgO directly from seawater or from bittern. Pre-concentration of seawater and dilution of bittern were found necessary to optimize the recovery and the purity of MgO. The MgO with the purity of 92.65% was produced from pre-concentrated seawater sample, and the same product with the purity of 91.21% was resulted from diluted bittern.

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