Effect of Dilution and Electrolysis Time on Recovery of Mg^{2+} As Mg(OH)$_2$ from Bittern by Electrochemical Method

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ABSTRACT

This research was conducted to study the effect of dilution and electrolysis time on the recovery of Mg^{2+} as Mg(OH)$_2$ from bittern by electrochemical method. The electrochemical process was carried out using 2-compartment electrochemical cell, connected by salt bridge prepared from NaCl suspended in gelatin. The experiment was carried out using nickel as cathode and carbon as an anode. The electrolysis process was carried out at a potential of 18 volts with dilution factors of 0, 2, 4, 6, and 8 times, and electrolysis time of 1, 2, 4, 6, 8, 10, and 12 hours. The results show that percent of conversion increased with dilution with the best result was obtained at 4x dilution factor and 4 hours electrolysis time with percent conversion of 85 % and purity of Mg(OH)$_2$ 91%.

Keywords: Bittern, 2-Compartment Electrochemical Cell, Mg(OH)$_2$, Dilution Factor, Electrolysis Time.

INTRODUCTION

Salt waste (Bittern), a by-product of salt production, is a potential raw material for the production of magnesium hydroxide since magnesium ions were found in high quantity together with several other components such as Na$^+$, K$^+$, and Ca^{2+}. Bittern has been used directly as a supplement beverage (nigari) [1], fish preservatives [2,3], and industrial waste coagulant [4–6]. Indirectly, bittern is used as raw materials such as in fertilizer manufacture[7–9], the raw material for production of potassium salt [10,11], and manufacture of various magnesium compounds, such as magnesium oxide (MgO) [12], magnesium sulfate [13] and magnesium hydroxide (Mg(OH)$_2$) [14].

Magnesium hydroxide, the intermediate of magnesium oxide, is used mainly in the pharmaceutical industry [15], antibacterial agent [16], refractory, water and wastewater treatment [17] and desulphurization of fuel gases [18]. The conversion process of Mg^{2+} in the bittern into Mg(OH)$_2$ is generally accomplished by the addition of chemical reagents such as dolomite [19], ammonium hydroxide (NH$_4$OH) [20], and sodium hydroxide (NaOH) [21]. In principle, Mg(OH)$_2$ can be obtained from bittern by an electrochemical method based on

electrolysis reaction. The OH⁻ ion formed at the cathode will then react with the Mg^{2+} ion to give $Mg(OH)_2$. This process indicates that the precipitation of $Mg(OH)_2$ will occur when the OH⁻ concentration has exceeded the concentration according to the solubility product of $Mg(OH)_2$. Formation of $Mg(OH)_2$ from bittern by an electrochemical method according to the reaction:

$$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)} \tag{1}$$

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

In the previous research [22], electrolysis of magnesium chloride solution and bittern using 2-compartment electrochemical cell connected by salt bridge prepared from NaCl suspended in gelatin, nickel as cathode and carbon as anode indicated that conversion percentages increase as the potential increase. But, in general, the yield of $Mg(OH)_2$ from bittern remains low. Park et al. [23] synthesized MgO nanoparticles using $Mg(OH)_2$ produced from bittern using precipitation method as precursors. The effect of bittern dilution was studied with a dilution factor of 5 and 10 times, showing that the purity of MgO produced from 10 times diluted bittern is higher than that of MgO produced from 5 times diluted bittern. It was reported that the MgO with a purity of 91% was produced from the 10 times diluted bittern. To gain more insight on the effect of dilution, in this study the bittern diluted with dilution factors of 0, 2, 4, 6, and 8.

Hsu et al. [24] study the effects of electrolysis time and electric potential on the formation of chlorine during seawater electrolysis. The results showed that electrolysis with a long time reduces the chlorine content produced and was detrimental to electrolysis efficiency, especially under high electric potential conditions. Therefore, it is necessary to choose the optimal time based on the electrolysis process with the cell potential used. The purposes of this study are to study the effect of bittern dilution and electrolysis time on the yield of $Mg(OH)_2$ produced and to determine the structure of the $Mg(OH)_2$ produced.
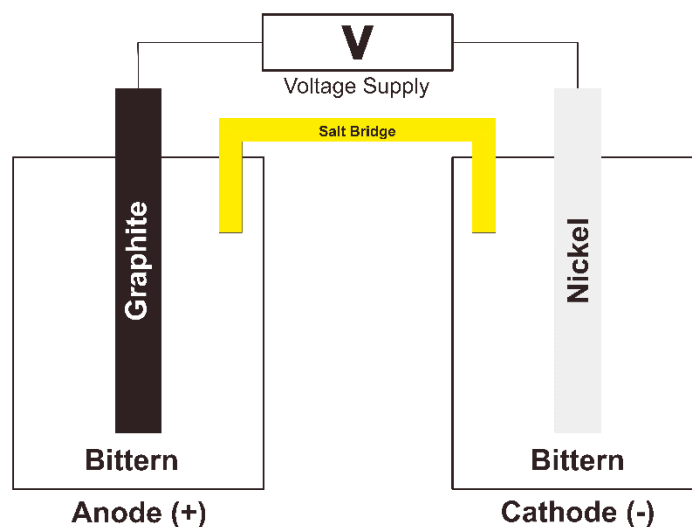
Figure 1. The schematic of electrochemical set-up used in the study.

EXPERIMENT
Chemicals and instrumentation

The bittern used in this study was obtained from Pamekasan, Madura island, while the gelatin powder and sodium chloride (NaCl) were obtained from Aldrich.

The electrochemical process was carried out using a 2-compartment electrochemical cell, as depicted in Figure 1, connected by salt bridge prepared from sodium chloride suspended in gelatin. The experiment was carried out using nickel as cathode and carbon as an anode. The cathode does not have specific requirements compared to anodes which require using inert electrodes (graphite, gold, and platinum) so that the anode is not oxidized and the use of cathodes can be replaced with other metals such as nickel. Nickel electrodes are stable and efficient electro-catalyst in alkali electrolytes, which have been widely used in the hydrogen gas production industry [25]. The experiment was carried out at controlled potential 18 Volt, room temperature and without adjustment of the pH of the bittern.

The concentration of Mg^{2+} in the bittern was determined by an inductively coupled plasma-optical emission spectroscopy (715 ES, Varian). Analysis of components in the final product was performed by X-ray fluorescence (Epsilon 3, PANAnalytical), morphology and particle size using SEM (FEI Inspect-S50) and identification of phase structures using X-ray diffraction (Expert pro, PANAnalytical) with Cu Kα radiation (λ = 1.5406 Å). The accelerating voltage and current used in this measurement were 40 kV and 30 mA, respectively. The diffractogram were recorded in the range of 10–80° in continue scan mode, scan speed 2 (deg/min).

Procedures for electrolysis

The electrolysis process was carried out at a potential of 18 volts with dilution factors of 0, 2, 4, 6, and 8, and electrolysis time of 1, 2, 4, 6, 8, 10, and 12 hours. After the electrolysis process, the product was filtered to obtain a solid product and washed three times with cold distilled water. The solubility of $MgCl_2$ and NaCl salts is very large in water, so it is easy to separate using distilled water. The use of cold distilled water was intended to optimize the removal of $Ca(OH)_2$ from $Mg(OH)_2$, since the solubility of $Ca(OH)_2$ is higher at a lower temperature.

Table 1. Physical and chemical properties of bittern

No.	Parameters	Units	Results
1	Color	-	Clear yellow
2	Density	^{O}Be	32
3	Temperature	^{O}C	27
4	Mg^{2+}	ppm	53372.45
5	Ca^{2+}	ppm	30153.96
6	K^{+}	ppm	57576.65
7	Na^{+}	ppm	17319.12

RESULT AND DISCUSSION
Effect of bittern dilution

Before electrolysis, the bittern was first analyzed to measure the concentration of Mg^{2+}. The results are shown in Table 1, showing that the bittern used has a clear yellow in colour, density 32 ^{o}Be, with Mg^{2+} content is 53372.45 ppm (mg/L) or 5.35% (w/v). However, other

metals ion also recorded; such as calsium 30153.96 ppm, potassium 57576.65 ppm, and sodium 17319.12 ppm, respectivelly.

The experimental procedure with bittern dilution was performed to determine the best bittern condition to produce high purity $Mg(OH)_2$, as a high bittern salinity could affect the electrochemical process [26]. Bittern dilution was done by adding distilled water to achieve the dilution factors of 2, 4, 6, and 8 times. The decrease of bittern density by dilution also indicates that the bittern salinity was reduced as shown in Table 2. Bittern with a dilution factor of 8 times has a density of 5 °Be. This value resembles the density of seawater which is around 4-5 °Be [12].

Table 2. The density of bittern dilution

Entry	Dilution Factor	Density (°Be)
1	0	32
2	2	18.5
3	4	10
4	6	7
5	8	5

Diluted bittern solutions were introduced into the cathodic and anodic compartments of 100 mL each. Electrolysis was performed with a potential of 18 volts for 10 hours. During the electrolysis process, it was observed that the color of the solution in the anodic compartment changed from clear to brownish yellow. This color change is associated with oxidation of Cl^- into Cl_2, according to the reaction:

$$2Cl^-_{(aq)} \rightarrow Cl_{2(g)} + 2e^- \qquad\qquad (3)$$

In the cathode compartment, a milky white deposit was formed. The formation of this deposit shows that at the cathode there is water reduction that produces OH^- ions, which then react with Mg^{2+} ions led to the formation of a solid $Mg(OH)_2$, according to the reaction (1) and (2).

The formation of the solid product (precipitate) implies that the concentration of $Mg(OH)_2$ has exceeded the solubility product constants (S) of $Mg(OH)_2$, which is 1.5×10^{-11}. The solid was collected by filtration using filter paper, and then washed with cold distilled water to optimize the removal of $Ca(OH)_2$ which was also produced during the electrolysis of the bittern. The washed $Mg(OH)_2$ was subsequently dried at 110 °C. The typical example of wet and dry $Mg(OH)_2$ are shown in Figure 2.

The study results obtained is summarized in Table 3. It is showed that bittern dilution can improve the purity of $Mg(OH)_2$ obtained. However, the recoveries of the Mg are practically the same, which is at around 85%, for all dilutions. Compared to the experimental result without dilution, it can be seen that dilutions led to improved $Mg(OH)_2$ purity and Mg recovery. As can be seen, the $Mg(OH)_2$ with the highest purity was obtained from the experiment using 4 times diluted bittern. For this reason, the 4 times diluted bittern was used for a further experiment, carried out to determine the optimum electrolysis time.

Figure 2. Mg(OH)$_2$ product (A) wet, (B) dry. "all dilution factors give an identical product morphology"

Table 3. The yield of product from electrolysis bittern with variation dilution factor.

| Entry	Dilution factor	Mg(OH)$_2$ Content (%)	Weight (g)	Conversion (%)
1	0	81.74	8.13	51.50
2	2	89.18	6.12	84.58
3	4	91.21	3.04	85.94
4	6	83.85	2.19	85.38
5	8	83.77	1.64	85.17

Optimum time determination

To determine the optimum electrolysis time, the experiments with different electrolysis times of time 1, 2, 4, 6, 8, 10, and 12 hours were undertaken at a fixed potential of 18 Volt and at a constant volume of 100 mL of the bittern. The experimental results are shown in Figure 3. It can be seen that, no product was formed during the electrolysis for 1 hour. It indicates that the concentration of OH⁻ was not sufficient for the production of solid Mg(OH)$_2$. A sharp increase in the mass of Mg(OH)$_2$ was observed with the electrolysis time up to 4 hours, followed by practical plat results up to 12 hour electrolysis time. From these findings, it is then concluded that the optimum time for conversion of bittern to magnesium hydroxide is 4 hours.

Characterization of Mg(OH)$_2$
Scanning Electron Microscopy (SEM)

To study the surface morphology of the Mg(OH)$_2$ obtained, a sample of Mg(OH)$_2$ produced from the experiment at the optimum time (4 hours) was characterized using SEM. The micrographs of the sample at different magnifications are presented in Figure 4.
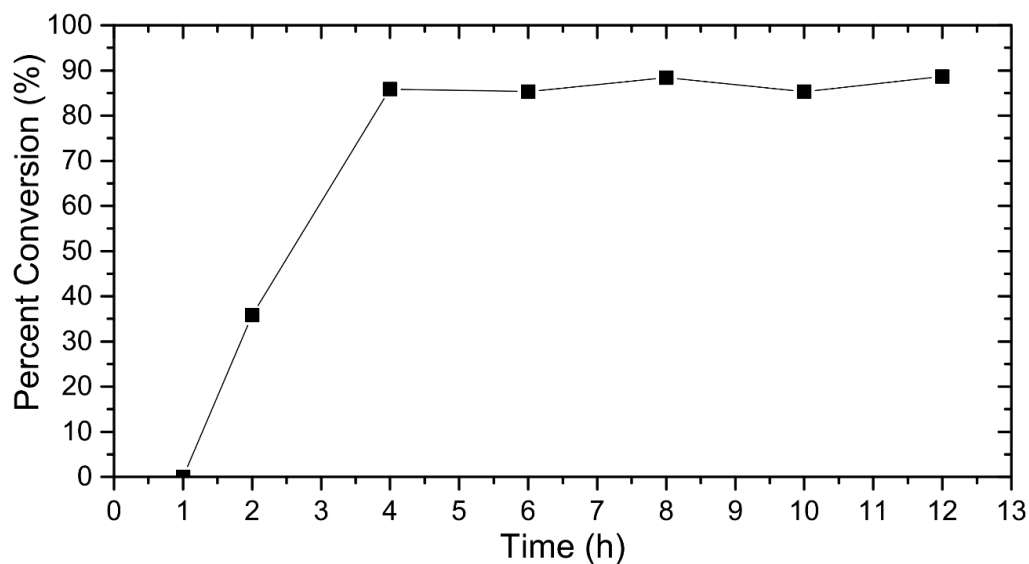
Figure 3. The effect of electrolysis times on the percent conversion of $Mg(OH)_2$ obtained from the 4 times diluted bittern.
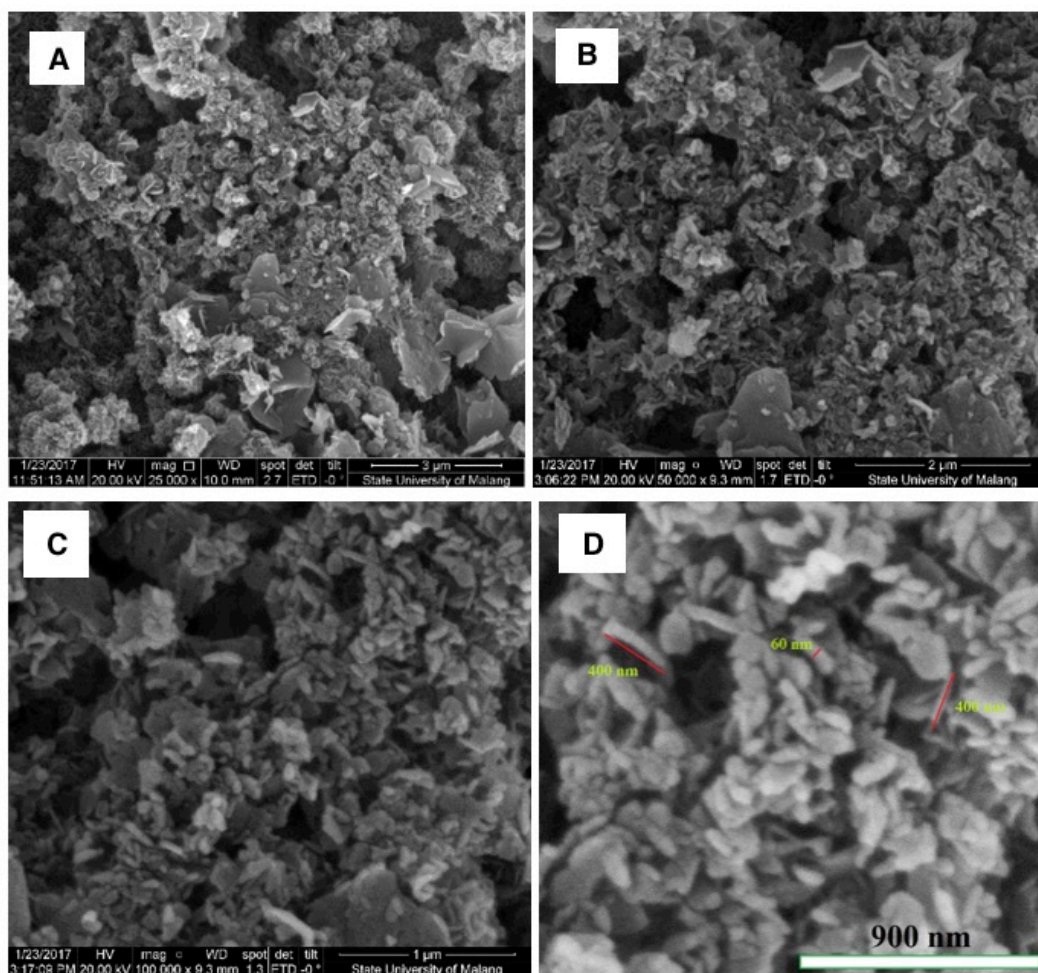

Figure 4. SEM image of $Mg(OH)_2$ (A) 25 kx, (B) 50 kx, (C) 100 kx, and (D) particle size.

As it can be seen in Figure 4, the surface morphology of the sample is marked by particles with different sizes and shapes, suggesting the presence of several phases in the sample. More evident characteristics of the sample surface are indicated in Figure 4D, in which it can be seen that the particles are an elongated layer with side lengths of 100-400 nm and thickness 20-65 nm. As a comparison, Hanlon, et al. [27], synthesized the $Mg(OH)_2$ through hydration of MgO in a multimode cavity microwave reactor, and SEM analysis of the $Mg(OH)_2$ produced, indicates the existence of hexagonal crystals as nano-layer with a side lengths of 100-300 nm and thickness 10-60 nm.

X-Ray Diffraction (XRD)

To identify the crystalline phases present in the sample, characterization using XRD technique was carried out for the sample obtained from the experiment with the optimum condition. The XRD pattern (diffractogram) of the sample is presented in Figure 5. As can be seen, the presence of crystalline phases in the sample is obvious as indicated by the existence of sharp peaks along with the 2θ range. With the aid of software Match program! Crystal Impact version 3, three crystalline phases were identified. They are $Mg(OH)_2$ with the standard peak 99-100-0055, $CaCO_3$ with the standard peak 96-901-5894, and NaCl with the standard peak 96-900-8679.
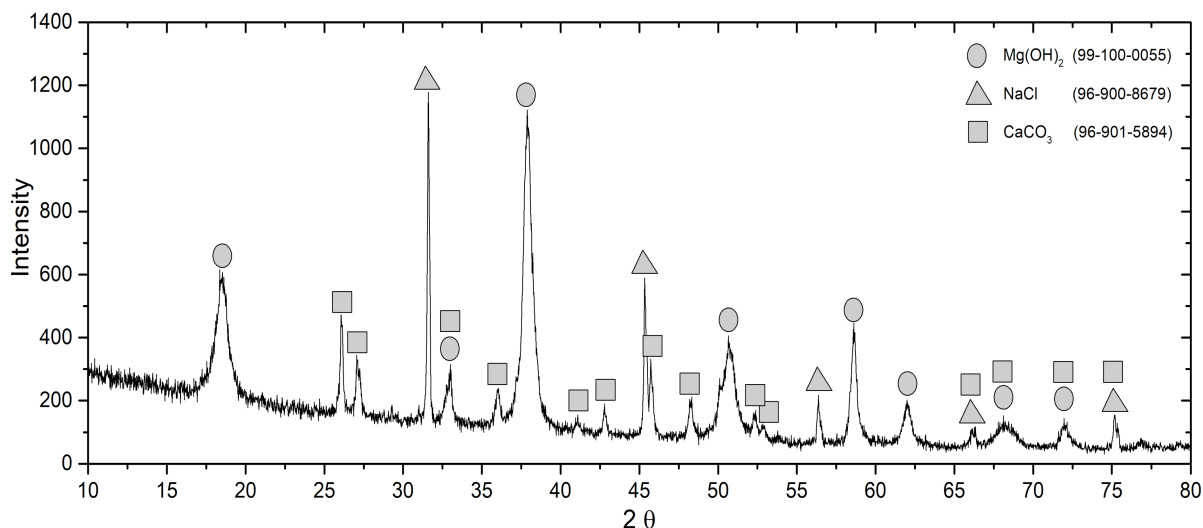
Figure 5. XRD pattern of $Mg(OH)_2$ obtained from bittern with a dilution factor of four and electrolysis time of four hours.

The emergence of peaks associated with crystalline NaCl and crystalline $CaCO_3$ implies that these two impurities were not completely removed from the $Mg(OH)_2$. Based on the nature of NaCl which is very soluble in water, the presence of NaCl phase in the product also indicates that this impurity is mot likely trapped in the molecular framework of $Mg(OH)_2$ strongly, making it very difficult to expel by washing with distilled water. The presence of crystalline $CaCO_3$, on the other hand, is most likely due to its insolubility in water, therefore cannot be removed by washing.

Another information is drawn from the XRD data with the aid of software Match program! Crystal Impact version 3 is the relative percentage of each phase identified in the sample, as presented in Table 4.

Table 4. Percentage of crystalline phase on the Mg(OH)$_2$ product

Crystal Phases		
Mg(OH)$_2$	CaCO$_3$	NaCl
63.84%	25.47%	10.69%

The experimental data presented in Table 4 suggest that the method developed in this study exhibits the appreciable potential to be developed further for production of Mg(OH)$_2$ from bittern or directly from seawater. However, it should be acknowledged that further exploration of the method is needed to improve the purity of Mg(OH)$_2$ produced.

CONCLUSION

The experimental results showed that the dilution of bittern can increase the conversion value. The optimum condition to obtain Mg(OH)$_2$ was at potential 18 volts, dilution factor 4 times, and electrolysis time 4 hour. The conversion value at maximum condition is 85.59% with purity 91.21%, and impurities still contained in Mg(OH)$_2$ are NaCl and CaCO$_3$.

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