Production of magnesium hydroxide and bromine from bittern

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Abstract

In this research, production of magnesium hydroxide and bromine from bittern has been performed using precipitation method. The Sodium hydroxide solution was added dropwise from a burette to 50 mL of bittern or Mg\textsuperscript{2+} solution. Preliminary precipitation experiments were carried out to adjust the super saturation release rate at which the primary nucleation was not dominant. After addition of sodium hydroxide solution, the reaction was stopped, the mixed solution allowed to stand for 5 minutes and the suspension in the crystallizer was filtered. The solid produced was oven dried at 110 oC for 24 hours. The magnesium hydroxide morphological was analyzed using Scanning Electron Microscope (SEM) and elemental composition analysis using energy-dispersive spectrometer (EDS). The filtrate was used in electrolysis experiment for production of bromine. The formation of bromine was analyzed using UV-Vis Spectrophotometer. The results were obtained magnesium hydroxide about 20% of the volume of bittern used as raw material. Magnesium hydroxide was analyzed using SEM and EDX, indicated the elemental composition of the sample: in which: magnesium 14%, oxygen 56%, and impurities. The electrolysis experiments demonstrated that the optimum conditions for production of bromine are potential of 5 volts, the optimum contact time of 45 minutes, and minimum concentration of Br\textsuperscript{-} of 15 mg/L.

1. Introduction

Salt waste (bittern), a byproduct of salt production, is a potential raw material for production of magnesium hydroxide and bromine, since magnesium and bromide ions were found in high quantity together with several minor components such as Ca\textsuperscript{2+}, Al\textsuperscript{3+}, Fe\textsuperscript{3+}, SO\textsubscript{4}\textsuperscript{2-}, and I\textsuperscript{-} (Cahyani, 2012). Traditionally bittern has been utilized in limited amount as isotonic and fertilizer (Sumada, 2007), as a source of liquid desiccant for use in solar-cooled greenhouses (Davies and Knowles, 2006), as a raw material for alkaline industry (Ayoub et al., 1991), additive for the removal of nitrogen and phosphate from waste (Lee et al., 2002), source of magnesium which is used as fertilizer struvite (magnesium ammonium phosphate) (Diwani et al., 2006).

Magnesium hydroxide, the intermediate of magnesium oxide, is used mainly in pharmaceutical industry, refractory, water and wastewater treatment and desulphurization of fuel gases (Bosster et al., 2003). Seawater is the main source for production of Mg(OH)\textsubscript{2} due to the presence of soluble salts of magnesium such as MgCl\textsubscript{2} and MgSO\textsubscript{4}. The concentration of magnesium ion is about 1272 ppm in seawater and about 30000 ppm in the end bitterns of sodium chloride production units from seawater (Rabadzhieva et al., 1997). Turek and Gnot (1995) investigated the effect of temperature on the precipitation of Mg(OH)\textsubscript{2} in the range 10–40°C when the precipitating agent was sodium hydroxide.
Bromine is a chemical with a very wide utilization in the industry for a variety of uses. For example, this element is an important reactant for hydrogenation reactions (addition of hydrogen atoms) to the compound of alkanes to alkenes into compounds, and brominated organic compounds or reactions. This element is also used as flame retardant in the environment (SGP Meeting, 2008). Bromine is found principally in seawater, salt lakes, and underground brines associated with oil. The concentration of bromide ion is about 0.84 ppm in seawater (Dave & Ghosh, 2005) and about 2.5 ppm in bittern (Anthony, 2006). Bromide ion is presently recovered from seawater, bittern and industrial waste containing the bromide ion (Nishihama, 2007).

In an attempt to take advantage of its availability and high content of Mg²⁺ and Br⁻ ions, in this study bittern was used as a source of Mg(OH)₂ and bromine. Production of Mg(OH)₂ was based on the reaction between Mg²⁺ and OH⁻ ions. Therefore, in this study the Mg(OH)₂ was produced by addition of sodium hydroxide solution into bittern, and after the solid Mg(OH)₂ was separated, the filtrate contains Br⁻ ion was subjected to electrolysis process in which the Br⁻ ions were oxidized to Br₂ at the anode side. For development of the method, the role of three electrochemical variables, potential, contact time, and the concentration of Br⁻ ions, was investigated.

2. Materials and methods

2.1 Materials

The chemicals used in this study, sodium bromide, sodium hydroxide, bittern, carbon electrode, and distilled water. And The equipments used in this study, glasware, electrolysis unit, SEM-EDS, and UV-Vis Spectrophotometer.

2.2 Methods

2.2.1 Precipitation of magnesium hydroxide

The sodium hydroxide solution was added drop-wise from a burette to the 50 mL bittern or Mg²⁺ solution. Preliminary precipitation experiments were carried out to adjust the super saturation release rate at which the primary nucleation was not dominant. Volume ratio was determined by volume comparisons bittern and sodium hydroxide. After addition of sodium hydroxide solution, the reaction was stopped, the mixed solution allowed to stand for 5 minutes and the suspension in the crystallizer was filtered. The filter cake was oven dried at 110 °C for 24 hours. The magnesium hydroxide morphological was analyzed using Scanning Electron Microscope (SEM) and elemental composition analysis using energy-dispersive spectrometer (EDS). The filtrate produced was conducted for obtaining bromine electrolysis. The electrolysis produced was analyzed using UV-Vis Spectrophotometer to identify the bromine content in the filtrate by absorbance at a particular wavelength.

2.2.2 Electrochemical for production of bromine

The parameter electrolysis method of experiments was conducted to study optimum potential, optimum contact time, and minimum bromide ion concentration effect on the effectiveness of the electrolysis process. The 5% sodium bromide were carried out in separating funnel with carbon electrode and then set up the potential. The experiments were carried out at potential variation, contact time variation, and bromide ion
concentration variation. The electrolysis produced was analyzed using UV-Vis Spectrophotometer to identify the bromine content in the filtrate by absorbance.

3. Results and discussion

3.1 Extraction magnesium hydroxide

The addition of sodium hydroxide to bittern produced white precipitate, which subsequently filtered and oven dried at temperature of 110°C for 24 hours and then crushed into powder as shown in Figure 1.

![Figure 1. Magnesium hydroxide: (A) wet magnesium hydroxide, (B) magnesium hydroxide after filtration, and (C) dry magnesium hydroxide.](image)

Extraction magnesium hydroxide was obtained about 20% (w/v) of the volume of bittern used as raw material. The magnesium hydroxide which has been smoothed SEM and EDX analysis to determine the morphology and composition of magnesium hydroxide produced as shown in the SEM analysis of data in Figure 2.

As the micrographs show the appearance of agglomerated particles with different size. The shape of particles produced in this study is in good agreement with the shape of particles produced in another study by reaction between sodium hydroxide and magnesium chloride (Henrist et al., 2003). Then the EDX analysis data is shown in Figure 3.

EDX measurement results indicate that magnesium hydroxide produced in this process is still contained impurities. Indicated the elemental composition of the sample: in which: magnesium 14%, oxygen 56%, and impurities. The result of measurement EDX showed that the magnesium hidroxide was produced, it was still impuritis.

3.2 Electrochemical for Production of Bromine

To determine the optimum parameter measurements using UV-Vis spectrophotometer measurements performed on a maximum wavelength of bromine compounds. The results of measurements of the maximum wavelength of bromine are presented in Figure 4.

Measurement of the maximum wavelength is obtained at a wavelength of 265 nm. Maximum wavelength will then be used to determine the concentration of bromine in determining the optimum potential, optimum contact time, and a minimum concentration.
of bromine. The optimum parameter measurement results using UV-Vis spectrophotometer is presented in Figure 5.

![Figure 5](image_url)

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<th>Series</th>
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<th>Norm. C [wt.%]</th>
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Figure 3. The results EDX spectra and table analysis.

![Figure 4](image_url)

Figure 4. The maximum wavelength of bromine compounds.

![Figure 5](image_url)

Figure 5. The optimum parameters for the potential and the contact time.

Electrolysis optimum parameters determined from the value of the highest concentration of each variable. The concentration obtained from the resulting absorbance
values changed in concentration by using a calculation Lambert-Beer law. The electrolysis experiments demonstrated that the optimum conditions for production of bromine are potential of 5 volts and the optimum contact time of 45 minutes. Then, to determine the minimum concentration of bromine is presented in Figure 6.

![Figure 6](image.png)

**Figure 6.** The UV-Vis spectra of minimum bromine concentration analysis.

The minimum concentration of bromide ion cannot be determined due to the results obtained from the calculation of the concentration is not stable. This is due to various factors that may be the potential is too high and the time is too long while the bromide ion concentration only in the ppm range, so that the resulting concentration is not appropriate. Therefore, used in determining the minimum concentration of bromide ions is based on the curvature of the UV-Vis spectra. Based on the spectra of the arch increasingly seen by the increase in the concentration of bromide ions is used. The higher the concentration of bromide ions, the spectra will be more curved the minimum concentration of Br⁻ ion of 15 mg/L.

The filtrate produced from magnesium hydroxide precipitation process used to obtain the bromine with electrolysis method. Electrolysis filtrate produces yellow-colored solution. The solution is bromine, such as those produced in the electrolysis of aqueous sodium bromide. The color comparison is shown in Figure 7.

![Figure 7](image.png)

**Figure 7.** The Comparison of the color sodium bromide and bittern (filtrate) solution.

Then, the result of the electrolysis filtrate the UV-Vis spectra measurements were taken using a UV-Vis spectrophotometer. The UV-Vis spectra of sodium bromide compared with the bittern (filtrate). The Comparison of the UV-Vis spectra shown in Figure 8.

Figures 7 and 8 indicate that the result of the electrolysis of the bittern (filtrate) containing bromine. Bromine is indicated on the yellow color of the solution of the bittern
(filtrate) as in the electrolysis of sodium bromide. The UV-Vis spectra showed the presence of bromine at a wavelength of 265 nm.

![UV-Vis spectra](image)

**Figure 8.** The Comparison of the UV-Vis spectra of sodium bromide and bittern (filtrate).

### 4. Conclusion

The results obtained indicated that magnesium hydroxide and bromine can be produced from bittern, using precipitation method for production of Mg(OH)_2 and electrolysis method for production of bromine.

### References


