Recovery of high purity sodium chloride from seawater bittern by precipitation-evaporation method

Jumaeri*, F W Mahatmanti, E F Rahayu, D Qoyyima, and A N K Ningrum
Department of Chemistry, Universitas Negeri Semarang, Indonesia

*Corresponding author: jumaeri.unnes@gmail.com

Abstract. Seawater bittern is a liquid that still exists after most of the NaCl has crystallized in the production of salt from seawater. The main components of the liquid are MgCl$_2$ and NaCl. This study aims to recover the NaCl present in bittern through the precipitation method with NaOH and evaporation. The initial stage of this research was collection of bittern in the salt production process in a salt pond. The obtained bittern samples were then added with NaOH to precipitate the MgCl$_2$ components as Mg(OH)$_2$ and leave NaCl as filtrate. The precipitate and the filtrate were separated by filtration. The obtained NaCl filtrate is then evaporated to obtain high purity NaCl. The product obtained was then determined the NaCl contents by argentometric titration. NaCl crystal was characterized using FTIR spectroscopy XRD spectroscopy, and Scanning Electron Microscope (SEM). The recovery results showed that the NaCl obtained had a high purity of 98.75% w/w and yield 30.45%. The IR spectra and diffractogram obtained showed compatibility with the characteristics of the reference NaCl.

1. Introduction
Salt productions tend to increase in line with the increasingly growth of industry and food need. The total national salt demand in 2015 reached 3.7 million tons and in 2019 it is estimated to reach 4.4 to 4.6 million tons [1]. In the production of salt from seawater, besides producing NaCl as the main product, it also produces residue (waste) in the form of bittern [2] Seawater bitterns are obtained in the desalination process and the production of sea salt where large quantities of bitterns and brine are produced, either as a by-product or as a waste product [3]. Bittern contains various ions such as Mg$^{2+}$, Ca$^{2+}$, K$^+$, Na$^+$, with the content of Mg ions is quite dominant [4]. The compounds MgCl$_2$, NaCl and KCl are the three main components of the bittern. For each ton of sea salt produced, approximately one cubic meter of bittern is obtained and is available for further processing [5]. Bittern is a viscous liquid obtained after harvesting sea salt [6] with a composition of 35% being NaCl [7]. Therefore, it is necessary to try to use bittern by processing it into a more useful material.

In recent years, bittern has been widely used as a precursor for the preparation Mg(OH)$_2$ and MgO through the precipitation method. In the precipitation method, a reaction occurs in which Mg(OH)$_2$ is precipitated from a saline solution using a precipitating agent, usually a strong base such as ammonia [8-9] or NaOH [10-11]. The reaction of bittern precipitation with NaOH and NH$_3$ in water is presented in equations (1) and (2), respectively. Through filtration, magnesium oxide precipitates Mg(OH)$_2$ and NaCl filtrate will be obtained.

\[
\begin{align*}
\text{MgCl}_2(\text{aq}) + 2 \text{NaOH}(\text{aq}) & \rightarrow \text{Mg(OH)}_2(\text{ppt}) + 2 \text{NaCl} (\text{aq}) \quad (1) \\
\text{MgCl}_2(\text{aq}) + 2 \text{NH}_4\text{OH}(\text{aq}) & \rightarrow \text{Mg(OH)}_2(\text{ppt}) + 2 \text{NH}_4\text{Cl} (\text{aq}) \quad (2)
\end{align*}
\]
When the precipitate Mg(OH)$_2$ was calcinated will produce MgO solid, while filtrate NaCl by evaporation will produce NaCl crystal. Therefore, the use of bittern not only for synthesis MgO but also simultaneously for recovery NaCl. These two materials have received much attention due to their unique and functional properties. Sodium chloride (NaCl) is widely used in the chemical industry, which includes food, pharmaceuticals, caustic soda, and soda ash needed for petroleum refining, petrochemistry, organic synthesis, glass production, etc. Approximately 60 percent of the world's salt production is used in the chemical industry [12]. Magnesium hydroxide, Mg(OH)$_2$, is also used as an antimicrobial [13] and a polypropylene composite filler [14].

Based on equation (1), the by-product NaCl will be increase as long as to increase the transformation bittern to Mg(OH)$_2$ and MgO. In the reaction sodium chloride (NaCl) not only as the reaction product, but it also exists in the precursor of the bittern used. The filtrate in this process can be evaporated effectively to produce NaCl crystals. Research on the use of bittern has been done to obtain MgOH$_2$ and MgO through many researchers. However, there has not been much of a by-product reprocessing to obtain NaCl. The present research will be studied the recovery of NaCl obtained in the precipitation seawater bittern using NaOH as a precipitator. The characteristics of the resulting NaCl and the effect of the mixture volume ratio, viscosity, and bittern type were also studied in this research.

2. Methods

2.1. Materials and equipment

The equipment used includes a set of glassware, Baumemeter, pH 1-14 stick indicator, Whatman filter paper, Oven Memmert 300 °C, muffle furnace Thermoline 1400 °C, FTIR Perkin Elmer Spectrum Version 10.03.06, ICP OES Optima 8300, XRD BRUKER 6000 D2 Phaser, Scanning Electron Microscope (SEM) Phenom Pro X desktop SEM with EDX, and a balance. The materials used include seawater bittern from salt ponds, NaOH, AgNO$_3$, K$_2$Cr$_2$O$_7$, and HCl. All the chemical used is E-Merck production, pro-analysis grade.

2.2. Preparation bittern and recovery NaCl by precipitation method

Bittern samples were taken from salt ponds in Kaliori and Lasem, Rembang. Before being reacted with NaOH, the bittern samples, which were already available in jerry cans, were left overnight to precipitate the solid impurities. Furthermore, bittern characterization was carried out which included viscosity, pH and composition of the constituent elements.

The bittern precipitation procedure refers to the modified method previously performed by Mustafa and Abdullah [6]. A total of 25 mL of bittern with varying viscosities (28, 29, 30, and 33 °Be) were put into a 100 mL polyethylene bottle. The solution was added to the 1 M NaOH with various volumes of 50, 75, and 100 mL. For each composition, the volume variations were carried out each within 30 minutes, then left overnight. Furthermore, the pH of the filtrate is adjusted until pH 7. After being left overnight, the mixture is filtered to obtain the filtrate and solids. Furthermore, the resulting filtrate at the end of the precipitation process is evaporated to obtain NaCl crystals. The solid NaCl is then dried at a temperature of 110 °C for 2 hours. The obtained MgO and NaCl products were characterized using XRD, IR, SEM. The content of NaCl was determined by the argentometric titration method using AgNO$_3$ solution.

3. Result and discussion

3.1. Characterization of Seawater Bittern

Bittern samples obtained from salt ponds before being used for the manufacture of MgO and NaCl, were characterized first for their chemical-physical properties. The results of characterization of seawater bittern samples at several viscosities (°Be) including elemental composition and pH are listed in Table 1. The result showed that the main content all of seawater bittern samples are Na, Mg, K, and Ca, which is similar results were also shown by previous studies [1, 16].
### Table 1. Chemical composition of seawater bittern

| Viscosity of Bittern (°Be) | Composition (mg/L) | pH |
|---------------------------|--------------------|----|
|                           | Na     | K     | Mg    | Ca    |
| 28                        | 19786.1 | 217.0 | 13804.4 | 203.7 | 6 |
| 29                        | 19128.7 | 359.4 | 14931.2 | 158.2 | 6 |
| 30                        | 18962.6 | 302.8 | 15051.9 | 287.6 | 6 |
| 33                        | 18207.9 | 266.9 | 14973.9 | 411.8 | 6 |

The high content of Na and Mg, indicated that the bittern still contained the high both NaCl and MgCl₂ compound, which can be recovered to find NaCl and Mg(OH)₂ by precipitation. The all of the bittern samples indicate slightly acid, pH = 6, which is related to the high content of MgCl₂.

3.2. Result of recovery NaCl from seawater bittern

3.2.1. Effect of types bittern. In this study, several types of bittern were used with different levels of viscosity. The volume of bittern and NaOH used was 25 mL and 75 mL respectively. All of them used pro analysis NaOH as a precipitating material, except for BF28T, using technical NaOH. Bittern samples 28 °Be came from salt ponds using HDPE, while bittern 29 °Be comes from salt ponds without HDPE. The resulted and yield of NaCl obtained through precipitation and evaporation processes are listed in Table 2. The used volume ratio of bittern: NaOH is 1: 3 and NaOH concentration 1mol/L. BS33, BF28, and BF28T were bittern from HDPE pond, while BG 29 was bittern from pond without HDPE. The number 28, 29, 33 indicate the bittern viscosity. The type of bitterns affects the NaCl yield. Bittern from ponds without HDPE produced the smallest NaCl yield, due to the presence of mud impurities in the pond.

### Table 2. Yield of NaCl from various types of bittern

| No | Bittern | NaCl resulted (g) | Yield (%) |
|----|---------|-------------------|-----------|
| 1  | BS33    | 7.268             | 29.07     |
| 2  | BG29    | 5.349             | 21.39     |
| 3  | BF28    | 7.184             | 28.74     |
| 4  | BF28 T  | 7.622             | 30.49     |

3.2.2. Effect of reagent composition on the amount of NaCl product. The resulted NaCl obtained from bittern in various ratio volumes listed in Table 3. NaCl products as listed in Table 3 for bittern samples from HDPE ponds showed a higher yield, yield 22.37-28.74%, than bittern from salt ponds without HDPE (21.39%). This can occur because of the presence of sludge impurities in the ponds without HDPE in the salt production process through the evaporation of seawater. The results of measuring NaCl levels using the Argentometric method for volume ratio 1:2 are 97.89 and 96.50 %, respectively for bittern from HDPE pond and without HDPE pond. The NaCl levels obtained from bittern from HDPE pond are higher than without HDPE pond. This happens because of the impurities that exist in HDPE pond less than in a pond without HDPE. As for those who use technical NaOH as a precipitator, the NaCl content is the lowest, which is 93.5 %.

### Table 3. Yield of NaCl on various the volume ratio of bittern : NaOH

| No | ratio | Bittern in pond with HDPE | Bittern in pond non HDPE |
|----|-------|---------------------------|--------------------------|
|    |       | Amount (g) | Yield (%) | Amount (g) | Yield (%) |
| 1  | 1:1   | 13.18 | 26.36   | 10.03   | 20.06   |
| 2  | 1:2   | 7.45  | 22.37   | 6.95    | 20.87   |
| 3  | 1:3   | 7.184 | 28.74   | 5.349   | 21.39   |
3.3. Infrared spectra of NaCl resulted from bittern precipitation

Infrared spectra of recovery product NaCl from some seawater bittern with volume ratio 1:2 are listed in Figure 1 and a summary of the absorption peak is shown in Table 4.

![Figure 1](image)

**Figure 1.** IR spectra of recovery NaCl: bittern from pond with HDPE (NaCl F2), without HDPE (NaCl G2) and using NaOH technical as precipitator (NaCl T)

**Table 4.** Main infrared spectra of NaCl resulted

| Puncak | NaCl F2 | NaCl G2 | NaCl T | Sea salt* | Lake salt* |
|--------|---------|---------|--------|-----------|------------|
| 1      | 3783.35 | 3700.06 | 3839.42| 3851.97   | 3851.97    |
| 2      | 3451.38 | 3413.91 | 3448.35| 3410.03   | 3434.61    |
| 3      | 2102.98 | 1642.94 | 2361.42| 2360.16   | 2359.90    |
| 4      | 1633.08 | 1124.01 | 1637.96| 1635.73   | 1635.64    |
| 5      | 1111.82 | 583.35  | 1110.69| 1124.58   | 1102.65    |
| 6      | 618.37  | 454.86  | 617.41 | 605.86    | 604.17     |

* Sea salt dan Lake salt data from [15]

Based on Figure 1 and Table 4, the three NaCl products and two types of salt (sea salt and lake salt obtained in previous studies, [15]) show the similarity of absorption peaks at wave numbers around 3400, 1635, 1100 and 605 cm\(^{-1}\). The absorption band in the area around 3440 - 3450 and 1630 - 1650 cm\(^{-1}\) can be related to the stretching and bending vibrations of the HOH water molecule. The absorption bands in the 1100 and around 600 cm\(^{-1}\) regions correspond to the typical absorption of Na-Cl.

3.4. Diffraction patterns XRD of NaCl resulted from bittern precipitation

The XRD diffraction patterns of recovered NaCl products from several seawater bittern samples obtained in this study are listed in Figure 2. Based on Figure 2, NaCl products from various bittern using pro-analysis NaOH (NaCl D, F2 and G2) show almost the same diffraction pattern. NaCl D is NaCl from bittern 33 °Be with volume ratio bittern : NaOH = 1:4.

![Figure 2](image)

**Figure 2.** Diffraction pattern of NaCl products from various types of bittern
The 2 theta values for the diffractogram peaks of the NaCl product were similar with the NaCl reference from JCPDS 78-0751 [16], viz at 2 theta: 27.42; 31.76; 45.54; 56.59; 66.37; 73.23; 75.46°. For NaCl which uses technical NaOH in the precipitation process (NaCl T7), it appears that the new peak is different, namely at 2 theta 19.12 with a relative intensity of 38.8% and other degree values as impurities. This occurs due to the use of technical NaOH in the bittern precipitation process.

3.5. **Image SEM and SEM EDX NaCl resulted from bittern precipitation**

Image of SEM and SEM EDX from NaCl recovery resulted from bittern precipitation in this study are listed in Figure 3.

![Image](image.png)

**Figure 3.** Image scanning electron microscopic of recovery NaCl: (a) using NaOH pro-analysis grade (b) using NaOH technical grade (c) elements counts of SEM EDX figure 3.b

Based on the SEM and SEM EDX images in Figures 3, it shows the formation of cube crystals from NaCl and the other crystals which are impurities. In the use of pro analysis NaOH obtained NaCl with less impurities than technical NaOH. Table 5 listed the element content of NaCl recovered by using NaOH technical which obtained from SEM EDX. The presence of this impurity is indicated by the chemical composition of NaCl FT obtained, NaCl 86.14% and the presence of elements O, K, Br and S which reached 13.86%, as shown in Table 5. We predicted existing impurities in NaCl recovery products are related to the presence K⁺, Br⁻, SO₄²⁻ ions in bittern sample and the use of technical NaOH.

**Table 5.** Element content NaCl

| Concentration | Na     | Cl     | O      | K      | Br     | S      |
|---------------|--------|--------|--------|--------|--------|--------|
| Atomic (%)    | 54.43  | 31.05  | 10.49  | 1.69   | 1.29   | 1.11   |
| Weight (%)    | 45.96  | 40.44  | 6.17   | 2.34   | 3.78   | 1.31   |

The SEM EDX analysis results are in accordance with the diffraction patterns of NaCl recovery which has been shown in Figure 2. On the diffraction patterns were obtained the presence of a diffractogram peak which is not included in the NaCl diffractogram.

4. **Conclusion**

The recovery results showed that the NaCl obtained from the bittern precipitation had a high purity depend on the bittern type, NaOH concentration, the volume ratio of bittern to NaOH. For the volume ratio of bittern : NaOH 1:2, the content of recovered NaCl are 97.89% and 96.50%, and yield 22.37% and 20.87 % respectively for bittern from HDPE pond and without HDPE pond. On the using of NaOH technical as precipitant, content and yield the recovered NaCl reached 93.5 and 30.45% respectively. The IR spectra and diffractogram of recovery NaCl obtained show compatibility with the characteristics of the NaCl reference.
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