A Double Salt Formation from Seawater Bittern and Ammonium Sulfate

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ABSTRACT

Seawater bittern, a huge reserve containing numerous mineral materials, is an essential source for producing various industrial salts. In this work, the formation of a double salt between magnesia abundant in the seawater bittern and ammonium sulfate was studied via SEM and EDX analyses. In the next step, to optimize the efficiency of the double salt separation, the effects of technological parameters such as concentration of reactants and their ratio, as well as reaction time and temperature, were investigated. Afterward, the design of the experimental method was utilized to quantify the influence of these parameters. Based on the validation of the obtained model according to statistical criteria, only the ratio of reactants and reaction time have been shown to have decisive roles in the yield of the double salt recovery. The optimal yield reached a value of about 95%, demonstrating the feasibility of the applied technique for further processes, i.e., industrial production.

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1. Introduction

Since seas and oceans cover about two-thirds of the Earth's surface [1, 2], seawater has been considered a large reserve that contains almost all elements found in the periodic table (even gold, silver, etc.) with different quantities [3, 4]. Usually, the production of NaCl via evaporation of seawater (3 – 5 °Bé, depending on different countries and continents) will result in a highly condensed mother liquid so call seawater bittern (SWB) (15 – 32 °Bé) which is usually treated as waste [5, 6]. However, plenty of valuable elements can be found in SWB, including chlorine, bromine, sodium, calcium, magnesium, and potassium, which have many critical applications in different fields, such as the food industry, chemical production, pharmaceuticals, etc. [7, 8]. Herein, the focus will be on the simultaneous separation of these ions in the form of double salts. This technique achieves certain advantages, especially for the fertilizer industry, since various minerals can be supplied for crops just by a single dosage of these double salts as multiple micronutrient fertilizers [9]. Besides, double salts are obtained as solid products, which are more favourable than liquid fertilizers due to the convenience of storage and transportation [10].

Conceptually, the double salt production method is mainly based on the interaction between ammonium sulfate (abbreviated as SA) and cation Mg^{2+}, which is the major portion of SWB. In general, both magnesium salt (i.e., $MgSO_4$) and SA can dissolve very well in water; for instance, the solubility of magnesium sulfate in an aqueous solution was found at a value of 35 g/100 g water (at 20°C) [11] while SA was reported with a value of 74.4 g/100 g water (at 20°C) [12]. On the contrary, the relatively low solubility of the salt-forming from those constituents can be calculated from a report by Daria *et al*. [13] that allows crystallizing of a solid double salt by adding SA into SWB solution. Upon this step, magnesium has been recovered from SWB as rich multiple micronutrient fertilizer sources, which can simultaneously supply magnesium, nitrogen, and sulfur elements [14]. For further applications, this salt can also be converted into SA and $MgSO_4$ under suitable conditions.

In order to crystallize the double salt, it is necessary to study the influencing factors such as concentration and ratio of reactants as well as reaction time and temperature. Subsequently, the Design of Experiment (DoE) method was applied in this work which was similar to the method described in the literature [15]. Briefly, preliminary trials were carried out to evaluate the influence of the individual parameters by gradually changing every single parameter while remaining the others at fixed values. Based on these results, the appropriate variable domains have been chosen to implement a full 2^k DoE plan which allows quantifying the yield of the double salt recovery as a function of affecting parameters.

2. Experiment

2.1. Chemicals and Apparatus

SWB 30 °Bé was provided by Vinh Hao Company (Vietnam), with chemical composition listed in Table **1** [13]. Ammonium sulfate and barium chloride dihydrate were purchased from Xinglong Co. (China) with more than 99% purity. Distilled water (Millipore) was used for analytical steps. Eriochrome black T (Merck) was used as an indicator in titration analysis.

Analytical equipment was used, including a scanning electron microscope - SEM (TM4000plus, Hitachi), and energy-dispersive X-ray spectroscopy - EDX (Quantax, Bruker). The temperature was controlled using a water bath (WNB, Memmert). The solid product was dried in a digital oven (Memmert UN55). The mass of the product was weighted by a balance (Sartorius Entris II). Besides, Hitachi U-2001 was used for UV-VIS analysis. A propeller was used to homogenize the fluid inside the reactor.

Table 1:   Chemical composition of Vinh Hao's SWB 30 °Bé [13].

Composition, g/L					
Cl^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	Na^+	K^+
139	105	0.20	24.5	6.2	7.9

Additionally, to determine the content of ions, further chemical analyses were conducted. Indeed, K^+ and Na^+ ions were analyzed via the X-ray fluorescence method (XRF), while Mg^{2+} ions were titrated by standard EDTA solution with the indicator Eriochrome black T (pH = 8-10). Besides, SO_4^{2-} the content was determined by measuring the opacity of the solution via a reaction with standard Ba^{2+} solutions. Finally, NH_4^+ content was determined by a spectrometric method when forming colored indophenols.

2.2. Experiment Procedure

The experiment was conducted as the following description: A volume of 100 mL SWB 30 °Be was placed in a 250 mL reactor, then SA solutions with different concentrations were added dropwise into the reactor. The system was immersed in the water bath to control the temperature (the interested temperature range was 30 – 60 °C, the temperature was measured inside the reactor), and the stirring speed was set at 250 rpm. After forming the double salt, phase separation was carried out by quick filtration. The obtained double salt was washed with 10 mL of cold distilled water to remove impurities and adherent ions, and then the product was dried at 60 °C for about 12 hours. A small amount of product was randomly collected for SEM and EDX analyses. Finally, from this obtained solid, the product mass was used to calculate the process yield, i.e., *H* value, which proves the efficiency of double salt recovery, as defined in Equation (1); $m_{obtained}$ was assigned to the mass of the obtained product and m_{total} referred to the total amount of the double salt available in SWB.

$$H = \frac{m_{obtained}}{m_{total}} \cdot 100 \ (\%) \tag{1}$$

Based on the process described above, the factors affecting the efficiency of the double salt separation were investigated, including (1) concentration of SA, (2) reaction time, (3) reactant molar ratio between SA and SWB, and (4) temperature. A full DoE for four parameters will be applied to describe the yield of recovery. Thus, there should be 2^4 = 16 experiments at this stage additionally, since each experiment will be repeatedly conducted three times to get the average results that will require a large number of experiments. Therefore, a simplification was applied to reduce the method to 2^3 = 8 experiments, as described in the next section.

3. Results and Discussion

3.1. EXD Analysis

For comparison purposes, commercial crystals of SA have been analyzed first. As seen in Figure **1a**, the EDX spectrum of SA showed the good quality of this compound since no trace of impurity was found in this reactant. A mass ratio of C:N:O:S elements were found at 5.73:10.06:16.58:67.63. It should be noted that carbon atoms appeared in this spectrum relating to carbon conductive glue, which was used to stick the sample onto the holder's surface of the analytical equipment. A similar approach was applied for the solid product, which was obtained from a reaction performed under the following conditions: (a) 5 mol/L SA solution; (b) 1:1 molar ratio of SA and SWB; (c) 90 mins reaction time, and (d) temperature at 30 °C. The EDX spectrum of this product was presented in Figure **1b** with a mass ratio of C:N:O:Mg:Mn at 5.49:6.63:64.70:5.42:1.68.
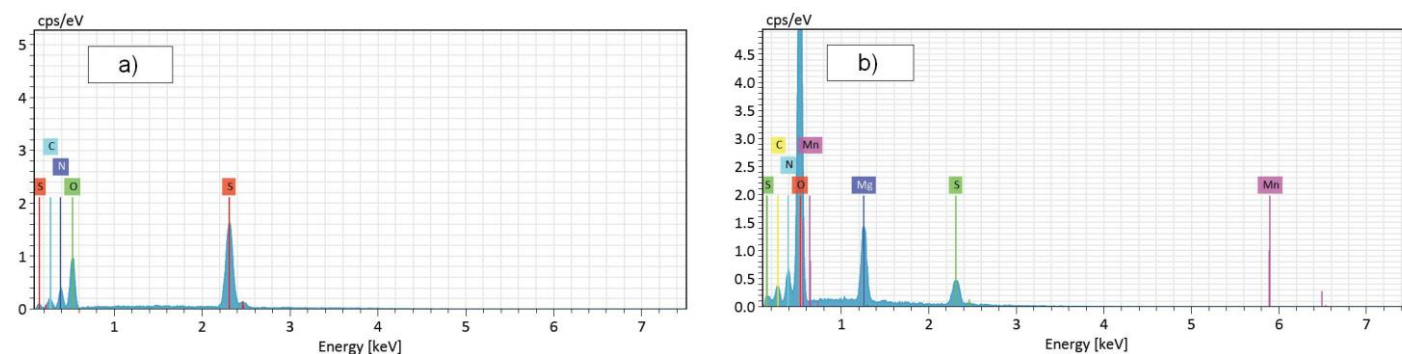

Figure 1: EDX analyses of (a) SA as a reactant and (b) the obtained product in the form of the double salt.

Regarding to the obtained product, a calculation based on the observed EDX spectrum showed that the molar ratio of atoms N:S:Mg:O is equal to 2:2:1:14. Therefore, the appropriate formula of this compound was approximated to $MgSO_4.(NH_4)_2SO_4.6H_2O$. This result gained a relatively good agreement with the literature [13] in which Daria *et al*. also proposed a formula of the double salt as $(NH_4)_2.Mg(SO_4)_2.6H_2O$.

3.2. SEM Analysis

Figure **2** proved that SA is a hygroscopic salt that quickly becomes damp and soft when exposed to a moist environment. In contrast, crystals obtained from the reaction between SA and SWB are relatively stable (under the same conditions as the case of SA), as shown in Figure **3**. Herein, crystal lattices were well developed to form distinguished crystal faces depicted in Figure **3**. Consequently, a combination between tetragonal prism and pyramid is typical for the crystal shape of the obtained product (Figures **3a** and **3b**). Besides, crystal size was found in a broad distribution of up to about 800 micrometers. Furthermore, evidence (see red-marked rectangular in Figures **3c** and **3d**) shows that the kinetic phenomena of this system seem to be complex due to the agglomeration and crystal growth simultaneously happening on the interface between contacted crystals to form stable secondary particles.
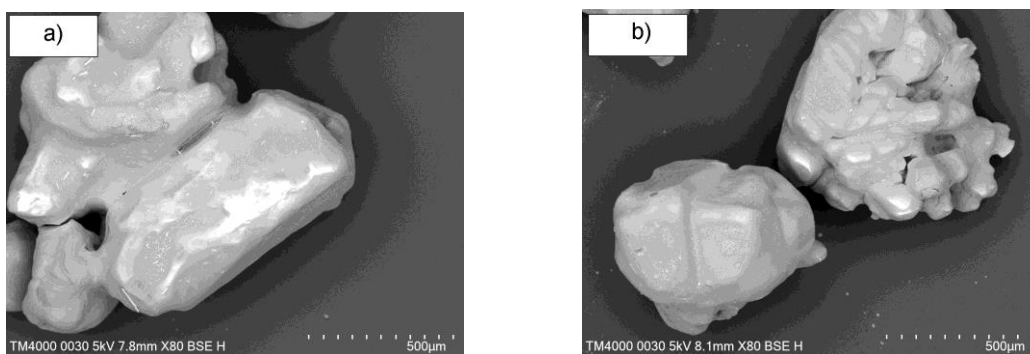

Figure 2: Two randomly collected SEM images of the commercial SA as the reactant show the hygroscopic property of SA.
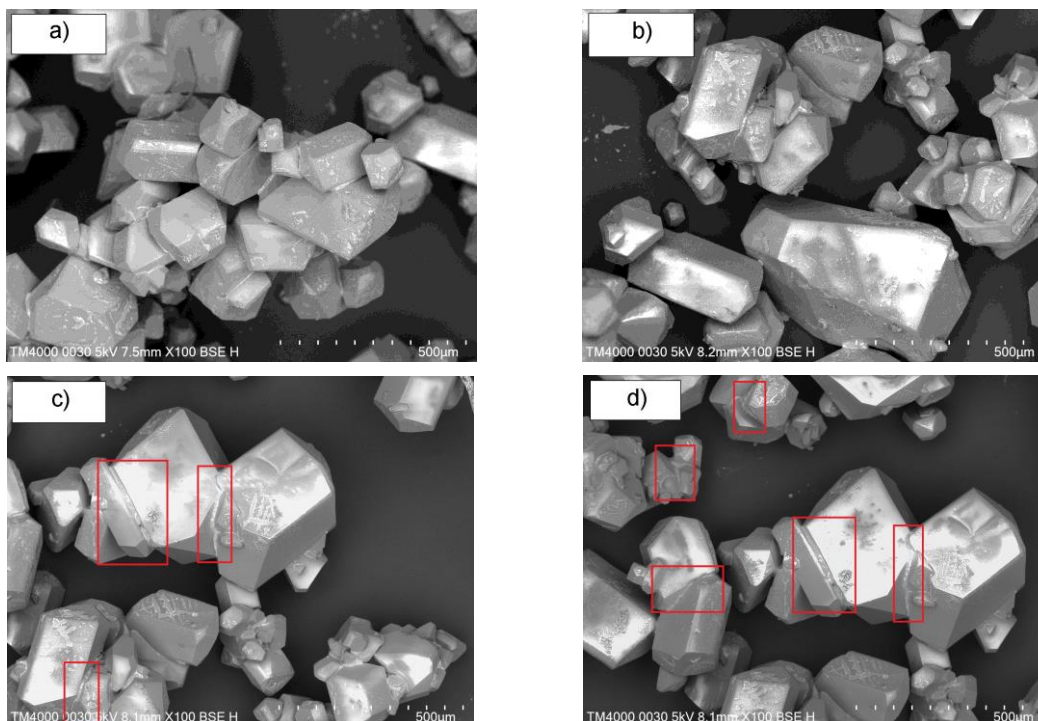

Figure 3: SEM images of the obtained double salt. (a) & (b) demonstrate typical crystal shape; (c) and (d) focus on red markers, which indicate stable secondary particle formation.

In short, a new compound has been found as the double salt when adding SA into SWB. This compound showed distinguished properties compared to the previous agents in crystal morphology and stability. Herein, the objective of this work is maximal recovery efficiency of this salt by controlling affecting technical parameters. The possible effects of these parameters will be examined in the next section.

3.3. Effect of Concentration of SA Solution

The first experiment was carried out in which only the concentration of SA solution was gradually increased from 3.8 to 5.4 mol/L. Meanwhile, the other parameters were kept constant, i.e., 90 minutes reaction time, reaction ratio of SA:SWB at 1, and temperature at 30 °C. The results are presented in Figure **4**.
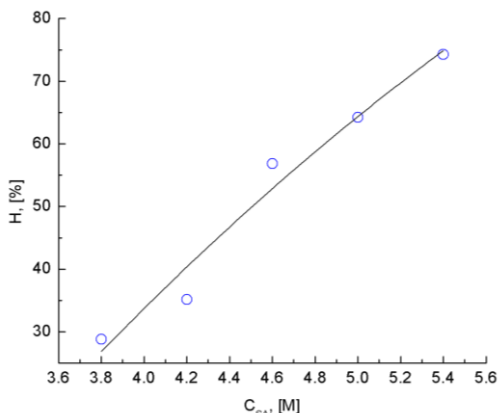

Figure 4: Effect of SA concentration on the double salt recovery efficiency, M and H denote concentration (mol/L), and the process yield (%) as defined in Equation (1).

SA concentration shows a strong effect on the process yield. Indeed, the process yield increases with increasing SA concentration. This relationship seems almost linear; for instance, increasing SA concentration from 3.8 to 5.4 mol/L leads to an increase in the process yield from 28.7 to 74.2%. Considering the equilibrium state of crystallization, the enhancement of the process yield can be explained due to the fact that when the concentration of the reactant increases, the system tends to establish a new equilibrium state in which more products will be formed (according to **Le Chatelier's Principle** [16]). In the DoE study, the concentration of SA was chosen as one of the investigated parameters.

3.4. Effect of the Reaction Time

A similar procedure to the previous section has been applied in this part, i.e., reaction time was increased from 15 to 180 mins while SA concentration, the ratio of reactants, and temperature were fixed at values of 5 mol/L, 1:1, and 30 °C, respectively. The results are shown in Figure **5**.

As seen in this Figure, the reaction time is the next important factor affecting the process efficiency. Indeed, the reaction time is directly proportional to the yield of double salt formation and separation. The process yield rapidly increases from 5.0 to 63.7% when the reaction time changes from 15 to 90 mins. After that, the yield does not increase significantly, even prolonging reaction time up to 180 mins. Besides, when the reaction time is significantly extended, the contamination of the product prevails. For the above reasons, the reaction time interval was chosen from 90 to 180 minutes for further study in the DoE section.

3.5. Effect of the Reactant Ratio

In this part, SA concentration was fixed at a value of 5 mol/L, the temperature remained at 30 °C, and the reaction time was 90 mins. Reactant ratio between SA:SWB was increased from 1 to 1.4, and the influence is presented in Figure **6**. Experimental results show that when gradually increasing the reaction ratio between SA and SWB, the efficiency of double salt production is also increased. From Figure **6**, we chose the reaction ratio

range from 1.2 to 1.4. If the remaining SA is too high, it will waste a certain amount of the SA reactant and therefore affecting the total cost of the process. Furthermore, the residual ammonium and sulfate content in the mother's liquor in large quantities could concern the removal of the other salts in the next steps.
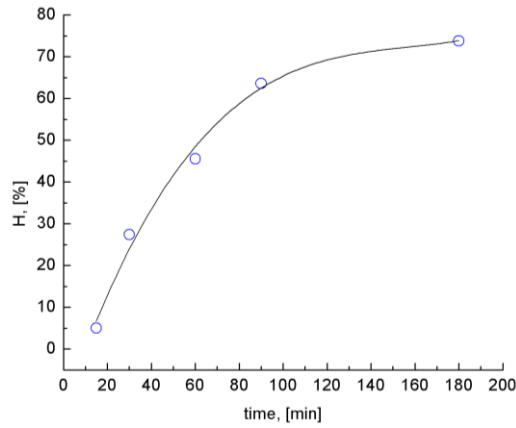

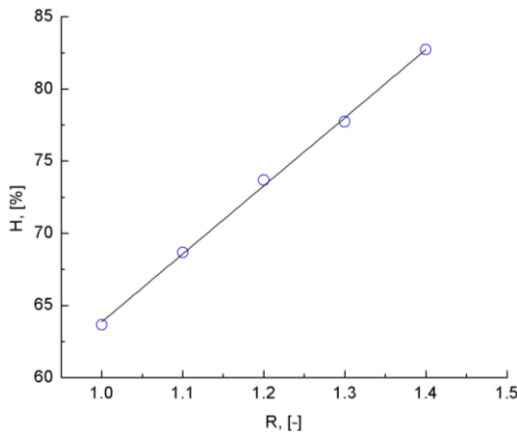**Figure 5:** Effect of reaction time on the process yield.

Figure 6: Effect of reactant ratio (R) between SA and SWB.

3.6. Effect of Temperature

Likewise to other above studies, the temperature was increased from 30 to 60 °C while SA concentration, reaction time, and reactant ratio were fixed at 5 mol/L, 90 mins, and 1, respectively. Data from Figure **7** have been analyzed to prove the role of temperature effects on the formation of the double salt.
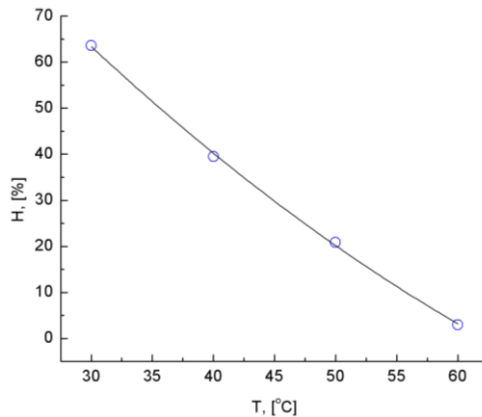

Figure 7: Effect of temperature on the process yield.

From the graph, it is found that temperature is inversely proportional to the yield of the double salt recovery. The reason is that as the temperature increases, the solubility of the solution also increases. That leads to the dissolute of the formed salt into the solution and, therefore, reduces the obtained salt in the solid phase. In short, increasing the temperature is not preferable for this salt production and also consumes energy. However, if the temperature is lowered, it could not only involve unwanted impurities [17, 18], but this condition is also relatively difficult to archive (on an industrial scale) in tropical countries such as Vietnam. Thus, the temperature effect will be eliminated by fixing this parameter at 30 ^{o}C for the next experiments.

3.7. Design of Experiment

Preliminary analyses in the previous part showed that three technological factors influenced the double salt recovery performance: Z_1– concentration of reactant SA (mol/L); Z_2– reaction time (mins); Z_3– reaction ratio between SA and SWB (-). The double salt recovery efficiency is denoted as y (%). In this section, only the final results were presented, and the calculation procedure was similar to the method described in the literature [15].

Table 2:   Matrix of the 2^3 DoE full factorial design.

Experiment N		Real Variable			DoE Variable			Objective Function y (%)
		Z_1	Z_2	Z_3	x_1	x_2	x_3	
2^k	1	5.4	180	1.4	1	1	1	96.54
	2	4.6	180	1.4	-1	1	1	93.99
	3	5.4	90	1.4	1	-1	1	88.93
	4	4.6	90	1.4	-1	-1	1	87.16
	5	5.4	180	1.2	1	1	-1	88.41
	6	4.6	180	1.2	-1	1	-1	87.41
	7	5.4	90	1.2	1	-1	-1	82.95
	8	4.6	90	1.2	-1	-1	-1	79.04

With the objective function y (%) assigned for the efficiency of the double salt recovery process, the process yield is expressed as Equation (2) which involves dependent and independent interactions of the three selected parameters.

$$y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{12}x_{12} + b_{13}x_{13} + b_{23}x_{23} \tag{2}$$

The compatibility of the mathematical model was validated. The meaning of the obtained parameters was checked, and the regression equation was examined with Fisher's criteria. After eliminating unaffecting parameters, the regression equation describing the double salt separation efficiency has the form of Equation (3). The central experiments (ratio at 1.3 and temperature at 30°C) were also carried out, resulting in an average value of $y_0 = 87.7\%$.

$$y = 88.05 + 3.53x_2 + 3.6x_3 \tag{3}$$

The regression model was obtained as a linear function which is graphically presented in Figure **8**. Thus, the maximal value of y will be obtained at the bounders of the studied regions. Under those conditions, the optimal efficiency of the double salt recovery process from SWB was calculated at 95.80%, corresponding to the influencing factors: concentration of SA at 5.4 mol/L; reaction time at 180 minutes; reactant ratio of SA:SWB at 1.4; and temperature at 30 ^{o}C. Based on the above optimizing factors, the actual efficiency was found at a value of 95.07%, which gained a good agreement with the calculated value.
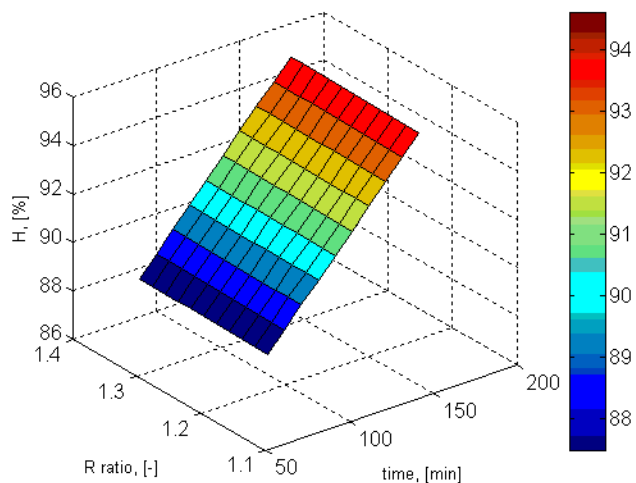
Figure 8: Response surface presents the process yield as a function of SA concentration and reaction time.

Finally, the chemical composition of the mother liquid was determined and shown in Table **3**. From the results, it can be seen that the concentrations of K^+ and Mg^{2+} ions are still relatively high. Thus, these ions can be further recovered by appropriate techniques. Besides, NH_4^+ content is also the target for the next step, which could be suggested to separate NH_4Cl by sublimation.

Table 3:   Content of ions in 100 mL of the mother liquor.

Ion	Na^+	K^+	Mg^{2+}	NH_4^+	SO_4^{2-}	Cl^-
concentration (g/L)	1.92	2.09	2.65	8.85	9.53	15.44

4. Conclusion and Outlook

By adding ammonium sulfate (SA) to seawater bittern (SWB), a double salt with low solubility was formed to crystallize this compound as relatively stable crystals. The obtained double salt was examined via SEM and EDX analyses which showed distinguished properties of the product compared to its constituents. The formula of the double salt was proven as $MgSO_4.(NH_4)_2SO_4.6H_2O$ that gained a good agreement with the literature.

A preliminary study on factors affecting the efficiency of double salt separation from SWB demonstrated the influences of technical parameters such as concentration of SA, the ratio of reactants, reaction time, and temperature. From that result, a full 2^3 DoE was modeled to evaluate the performance of double salt separation and to optimize the process yield. Based on the obtained Equation, the optimal conditions of the reaction were determined at the following parameters, including ammonium sulfate concentration at 5.4 mol/L, reaction time at 180 minutes, and reactant ratio between SA:SWB at 1.4.

For future works, from the analysis results relating to the mother liquor after recovering the double salt, it can be seen that the contents of the remaining ions in the solution, such as K^+, $Mg^{2+,}$ and NH_4^+, are relatively high. Thus, there is an opportunity to recover these valuable components by suitable methods such as sublimation of NH_4Cl or further crystallization of $MgCl_2$, etc.

Acknowledgement

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