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Conversion of Magnesium from Bittern with Sodium Phosphate Addition through Precipitation Process

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Abstract

Bittern, a by-product of the salt production process, contains high concentrations of magnesium ions, which have significant economic potential and use value in various fields. The objective of this study is to recover magnesium from bittern using sodium phosphate (Na_3PO_4) through the process of chemical precipitation. The reaction between magnesium and phosphate produces magnesium phosphate compounds, which are commercially valuable in the industrial and agricultural sectors. The present study analysed the effect of several process parameters, including pH, temperature and reaction time, on magnesium recovery efficiency. Optimum conditions were obtained at pH 9 with the addition of a 15% concentrated Na_3PO_4 solution. The precipitate formed was then characterised using X-Ray Fluorescence (XRF) to confirm the presence of magnesium phosphate. The findings demonstrate that this method facilitates the effective recovery of magnesium from bittern, exhibiting both high efficiency and good selectivity. This approach has the potential to provide a sustainable solution for the treatment of bittern effluent, whilst concomitantly producing environmentally friendly value-added products.
Keywords: *bittern, magnesium recovery, sodium phosphate, precipitation, magnesium phosphate*

Abstrak

Bittern, produk sampingan dari proses produksi garam, mengandung ion magnesium dengan konsentrasi tinggi yang memiliki potensi ekonomi signifikan dan nilai guna dalam berbagai bidang. Penelitian ini bertujuan untuk memulihkan magnesium dari bittern menggunakan natrium fosfat (Na_3PO_4) melalui metode pengendapan kimia. Reaksi antara magnesium dan fosfat menghasilkan senyawa magnesium fosfat, yang dikenal memiliki nilai komersial di sektor industri dan pertanian. Studi ini menganalisis pengaruh beberapa parameter proses, termasuk pH, suhu, dan waktu reaksi terhadap efisiensi pemulihan magnesium. Kondisi optimum diperoleh pada pH 9 dengan penambahan larutan Na_3PO_4 berkonsentrasi 15%. Endapan yang terbentuk kemudian dikarakterisasi menggunakan X-Ray Fluorescence (XRF) untuk mengonfirmasi keberadaan magnesium fosfat. Hasil penelitian menunjukkan bahwa metode ini memungkinkan pemulihan magnesium dari bittern dengan efisiensi tinggi dan selektivitas yang baik. Pendekatan ini berpotensi menjadi solusi berkelanjutan untuk pengolahan limbah bittern sekaligus menghasilkan produk bernilai tambah yang ramah lingkungan.
Kata Kunci: *bittern, pemulihan magnesium, natrium fosfat, presipitasi, magnesium fosfat*

1. Introduction

The development of the salt industry in Indonesia has steadily increased in recent years, in line with national food security programs and growing industrial demand. While the salt production process is relatively simple and commonly conducted in coastal areas, it also generates a liquid by-product known as bittern. Bittern is the residual brine left after salt crystallization, which still contains significant concentrations of valuable ions such as magnesium (Mg^{2+}), sodium (Na^+), chloride (Cl^-), and potassium (K^+) [1]. Despite its rich mineral content, bittern is often discharged directly into the environment without any further processing, leading to environmental concerns and underutilization of potentially valuable resources. there is about 1 m3/day of bittern generated from one of the salt industries in East Java for 10 tons/product [2].

Several studies have reported that the magnesium (Mg^+) content in bittern can exceed 28,867 mg/l [3], depending on the location and crystallization techniques used. One of the high-value compounds derived from magnesium is magnesium phosphate ($Mg_3(PO_4)_2$), a compound known for its use in the raw material for making fertilizers [4]. This has led to the agricultural sector's growing demand for phosphate-based fertilizers. However, domestic magnesium phosphate production in Indonesia is still limited and still largely dependent on imported raw materials. Therefore, it is imperative to identify alternative, abundant, and inexpensive local sources of magnesium. Bittern, which is a waste product from the salt industry and rich in magnesium, is emerging as a promising raw material that can be converted into magnesium phosphate through a simple chemical process so that it can be a valuable contributor in the future industry [5].

This study employs the chemical precipitation method to synthesize magnesium phosphate from bittern. Precipitation is chosen due to its operational simplicity, cost effectiveness, and minimal equipment requirements [6]. The reaction involves combining magnesium chloride extracted from bittern with sodium phosphate (Na_3PO_4), resulting in the formation of a magnesium phosphate precipitate [4]. Critical process variables such as pH and sodium phosphate concentration play a major role in influencing the yield and purity of the product. Previous research has demonstrated that precipitation of metal ions, including magnesium, is highly sensitive to pH levels. At low pH, magnesium remains dissolved as ions, while at excessively high pH, the formation of soluble complexes can prevent proper precipitation [7]. The concentration of sodium phosphate also influences the reaction equilibrium; insufficient phosphate leads to incomplete precipitation, while excess may result in undesirable by-products or increased solubility [8].

This study systematically investigates the effect of pH and Na_3PO_4 concentration on the precipitation of magnesium phosphate from bittern. Optimization is carried out using Response Surface Methodology (RSM) with a Central Composite Design (CCD) approach to determine the best experimental conditions for maximizing both product yield and magnesium phosphate content.

The aim of this research is to contribute to the development of green chemistry and circular economy principles by transforming waste bittern into a valuable and marketable product. Furthermore, the findings may serve as a foundation for scaling up the process and integrating it into industrial salt processing operations, enhancing sustainability and economic viability in the sector.

2. Research Methods

Preparation of Research Materials

A total of 1000 mL of bittern was transferred into a beaker glass and analyzed using Atomic Absorption Spectrophotometry (AAS) to determine its magnesium content [9]. To isolate magnesium, 7% NaOH solution was slowly added to the bittern without stirring and left to stand for 60 minutes to allow the formation of magnesium hydroxide ($Mg(OH)_2$) as a white colloidal precipitate. After sedimentation, the mixture was stirred at 250 rpm for 50 minutes to increase contact between Mg^{2+} ions and OH^- ions, enhancing the formation of $Mg(OH)_2$ [8]. The resulting precipitate was then filtered and washed with distilled water to remove chloride impurities that could interfere with the formation of magnesium phosphate.

$$MgCl_{2(l)} + 2NaOH_{(l)} \rightarrow Mg(OH)_{2(s)} + NaCl_{(l)} \quad \text{……………......…..(1)}$$

$$MgSO_{4(l)} + 2NaOH_{(l)} \rightarrow Mg(OH)_{2(s)} + Na_2(SO)_{4(l)} \quad \text{..………………..….(2)}$$

The filtered $Mg(OH)_2$ was dissolved in hydrochloric acid (HCl) to form a magnesium chloride ($MgCl_2$) solution. This step was carried out at 30 °C with stirring at 250 rpm for 50 minutes. The pH of the solution was adjusted to five different levels (8.0, 8.5, 9.0, 9.5, and 10.0) using NaOH or HCl, depending on the requirement of the experimental design.

$$Mg(OH)_{2(s)} + 2HCl_{(l)} \rightarrow MgCl_{2(l)} + 2H_2O_{(l)} \quad \text{…………………..(3)}$$

[10]

Precipitation Process

After the $MgCl_2$ solution was prepared and its pH adjusted to the target level, sodium phosphate (Na_3PO_4) was added at varying concentrations of 5%, 10%, 15%, 20%, and 25% (w/w). The reaction mixture was stirred continuously at 250 rpm for 50 minutes at a constant temperature of 30 °C to facilitate the reaction between magnesium ions (Mg^{2+}) and phosphate ions (PO_4^{3-}). This reaction resulted in the formation of magnesium phosphate ($Mg_3(PO_4)_2$) as a solid precipitate. After the reaction was completed, the precipitate was separated by vacuum filtration and then dried in an oven at 30 °C until a constant weight was obtained. The dried product was then weighed to determine the mass of magnesium phosphate formed.

$$3MgCl_{2(l)} + 2Na_3PO_{4(l)} \rightarrow Mg_3(PO_4)_{2(s)} + 6NaCl_{(l)} \quad \text{………..……...(4)}$$

[4]

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Analysis Method

Finally, The chemical composition and purity of the dried magnesium phosphate were analyzed using X-Ray Fluorescence (XRF). Additionally, the yield of the precipitation process was calculated based on the initial magnesium content in the bittern and the final mass of the recovered magnesium phosphate. These analyses were performed to evaluate the effectiveness of the precipitation process and to determine the influence of sodium phosphate concentration on the quality and quantity of the product.

Experimental Design and Optimization

This study employed a two-factor experimental design to investigate the effect of pH and sodium phosphate concentration on the precipitation of magnesium phosphate from bittern. The independent variables selected for optimization were the solution pH (ranging from 8.0 to 10.0) and the concentration of sodium phosphate (Na_3PO_4) added to the solution, which varied between 5% and 25% (w/w). The experimental matrix was designed using Response Surface Methodology (RSM) with a Central Composite Design (CCD) approach, facilitated by Design Expert Software version 13. This method allows for efficient evaluation of both the main and interaction effects of the variables on the response parameters. The responses measured were the yield of magnesium phosphate (%) and the gravimetric purity of the product (%). A total of 15 experimental runs were generated and analyzed to develop a quadratic model capable of predicting optimal process conditions [11]. The model's reliability and accuracy were evaluated using statistical parameters such as the coefficient of determination (R^2), analysis of variance (ANOVA), and lack of fit tests.

3. Results And Discussion

Initial Bittern Composition

The raw bittern sample used in this study was analyzed to determine its mineral content before undergoing the precipitation process. The analysis was conducted using AAS, titrimetri, and APHA standard methods. The results are summarized in **Table 1**.

Table 1. Preliminary analysis result of bittern content

No	Parameters	Units	Result	Methods
1	Natrium	mg/L	47134,8	AAS
2	Klorida	%	39,2	Titrimetri
3	Magnesium	mg/L	75553,2	AAS
4	Fosfat	mg/L	9,55	SM APHA 23rd Ed., 4500-P C, 2017

Source: Badan Standarisasi dan Pelayanan Jasa Industri Surabaya (2024)

Bittern analysis was conducted using the Atomic Absorption Spectroscopy (AAS) method. This method is used to determine heavy metal levels based on the principle of absorption of electromagnetic rays by metal atoms at certain wavelengths [9]. The titrimetric method is also used as a quantitative method. This process involves a standard solution and a titrated solution with the help of an indicator that shows the end point of the reaction through a color change [12]. In addition, the analysis of phosphate levels in bittern follows APHA guidelines. This standard is contained in the 23rd edition of Standard Methods for the Examination of Water and Wastewater 2017 published by the American Public Health Association [13].

The results indicated that the bittern contained a high concentration of magnesium (75553,2 mg/L), along with significant levels of sodium (47134,8 mg/L) and chloride (39,2%). The phosphate content was relatively low at 9,55 mg/L. These findings confirm that bittern is a potential raw material for magnesium-based product synthesis, particularly magnesium phosphate, given its abundant magnesium content.

Table 2. The results of XRF analysis of the concentration of Magnesium phosphate compounds in the variable addition of 15% concentration of sodium phosphate solution with pH 9**.**

Components	Concentration (%)
Magnesium	15
Fosfat	68,5
Kalsium	4,63
Kromium	0,15
Besi	0,17
Nikel	0,14

Source: Laboratorium Mineral dan Material Maju Universitas Negeri Malang (2024)

Based on **Table 2**, the results of XRF analysis show that at the addition of 15% sodium phosphate and pH 9, the magnesium phosphate compound formed has a main content of phosphate by 68.5% and magnesium by 15%. In addition, other elements such as calcium (4.63%), and traces of heavy metals such as chromium, iron, and nickel with concentrations below 0.2% were also detected. This indicates that these conditions not only result in a high primary composition, but also relatively low heavy metal contamination.

Effect of pH on Product Yield and Purity

The pH of the solution plays a crucial role in determining the extent of magnesium phosphate precipitation. The experiment showed that yield and product purity generally increased with pH, reaching optimal values around pH 9. At lower pH levels (pH 8–8,5), incomplete precipitation was observed, likely due to insufficient OH^- ions required for the formation of stable magnesium phosphate [14]. Meanwhile, at pH levels above 9,5 the product yield decreased slightly, potentially due to the redissolution of precipitates or formation of soluble magnesium complexes.

Table 3. The results and calculations of magnesium yield to magnesium phosphate on the weight of magnesium precipitate produced

pH	Na_3PO_4 concentration (%)	Precipitated magnesium content (%)	Yield of magnesium to raw material (%)
8	5	48.92076	52,105
9		74.50	67.35
10		73.27	42.04
8	10	73.81	53.28
9		75.81	71.80
10		75.81	56.78
8	15	77.12	76.38
9		77.27	87.10
10		76.27	71.80
8	20	74.49	54.47
9		76.13	81.77
10		74.40	68.89
8	25	75.92	60.42
9		74.96	75.83
10		74.83	64.24

The highest yield obtained was 87,10% at pH 9 with 15% sodium phosphate concentration, while the highest purity was 77,27% under the same condition. These values indicate that pH 9 is the most favorable condition for the formation of magnesium phosphate in this process.

Effect of Sodium Phosphate Concentration

Sodium phosphate acts as the phosphate ion donor in the precipitation reaction. The concentration of Na_3PO_4 was varied from 5% to 25% to determine its effect on product formation. The results showed a direct correlation between phosphate concentration and product yield up to 15%, beyond which the yield plateaued or slightly declined.

This trend suggests that 15% Na_3PO_4 provides sufficient phosphate ions for complete reaction with available Mg^{2+}. Higher concentrations may lead to oversaturation, reducing precipitation efficiency due to the formation of highly soluble phosphate species or undesired side reactions.

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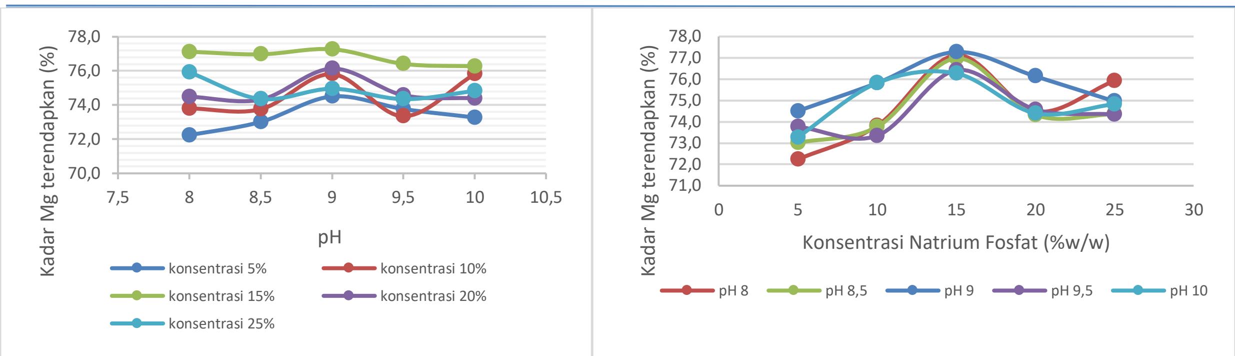

Figure 1. Relationship between magnesium content in the presence of pH change factors and Sodium Phosphate Concentration

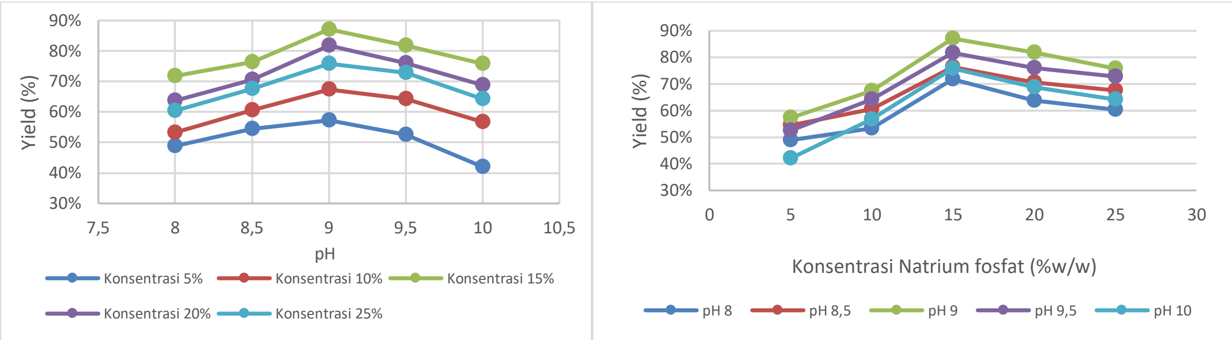

Figure 2. Relationship between Yield in the presence of pH change factor and Sodium Phosphate Concentration

Optimization Using Response Surface Methodology (RSM)

Optimization of process variables was carried out using Response Surface Methodology (RSM) with a Central Composite Design (CCD) approach. The analysis showed that pH and Na_3PO_4 concentration significantly affected the response variables, namely magnesium phosphate content and product yield. The resulting statistical model showed high coefficient of determination (R^2) values of 0.8727 for magnesium phosphate content and 0.9745 for yield, indicating an excellent model fit. The high R^2 value in product yield indicates a strong correlation between variables, where the pH factor of the solution and the addition of sodium phosphate concentration have a significant effect on the response of magnesium phosphate product content and yield [15].

Table 4. Anova analysis of quadratic models

Magnesium phosphate content response						
Source	***Std. Dev.***	***R^2***	***Adjusted R^2***	***Predicted R^2***	***PRESS***	
Quadratic	0.637	0.8727	0.8352	0.7574	13.14	*Suggested*
Source	***Std. Dev.***	***R^2***	***Adjusted R^2***	***Predicted R^2***	***PRESS***	
Model	47.28	5	9.46	23.3	< 0.0001	*significant*
Yield product response						
Quadratic	2.37	0.9745	0.967	0.9514	182.52	*Suggested*
Source	***Std. Dev.***	***R^2***	***Adjusted R^2***	***Predicted R^2***	***PRESS***	
Model	3657.84	5	731.57	130.11	< 0.0001	*significant*

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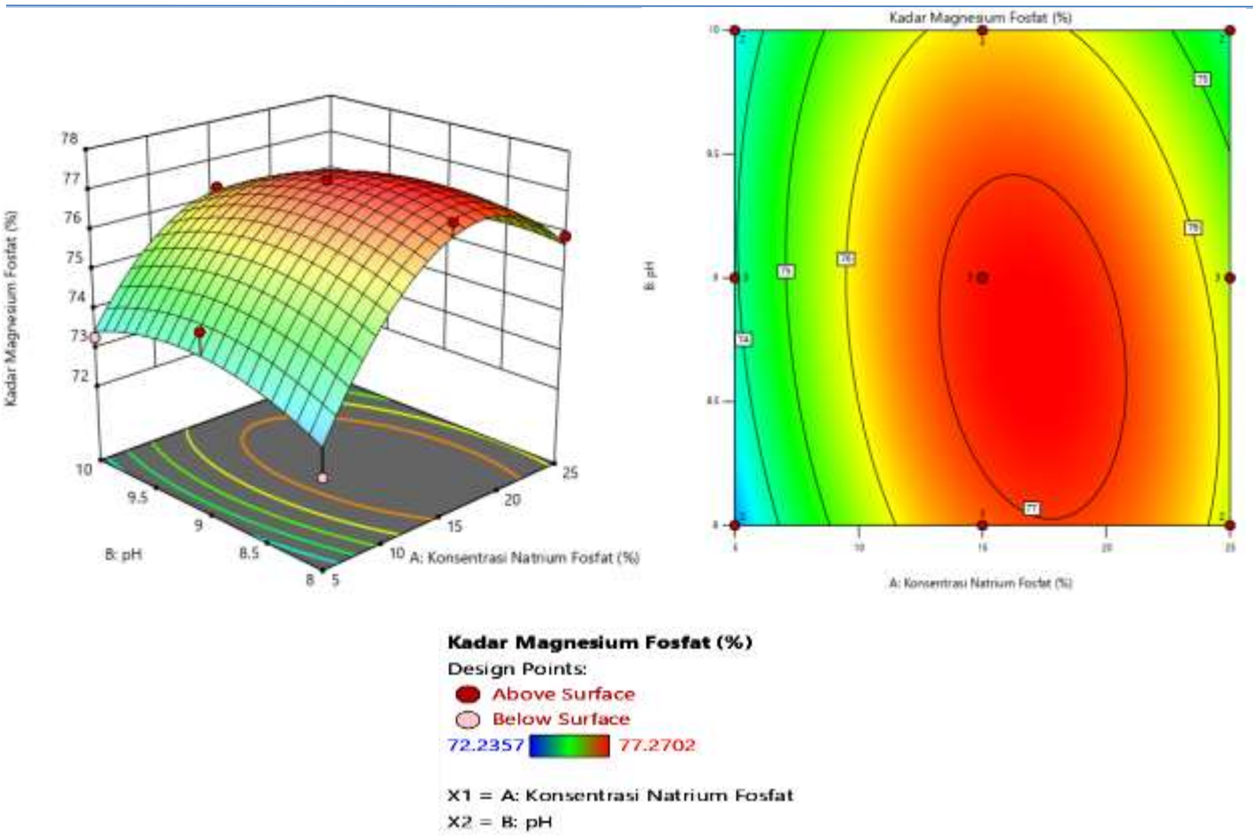

Figure 3. The 3D and Contour graphs of the effect of solution pH and sodium phosphate concentration on % magnesium phosphate content

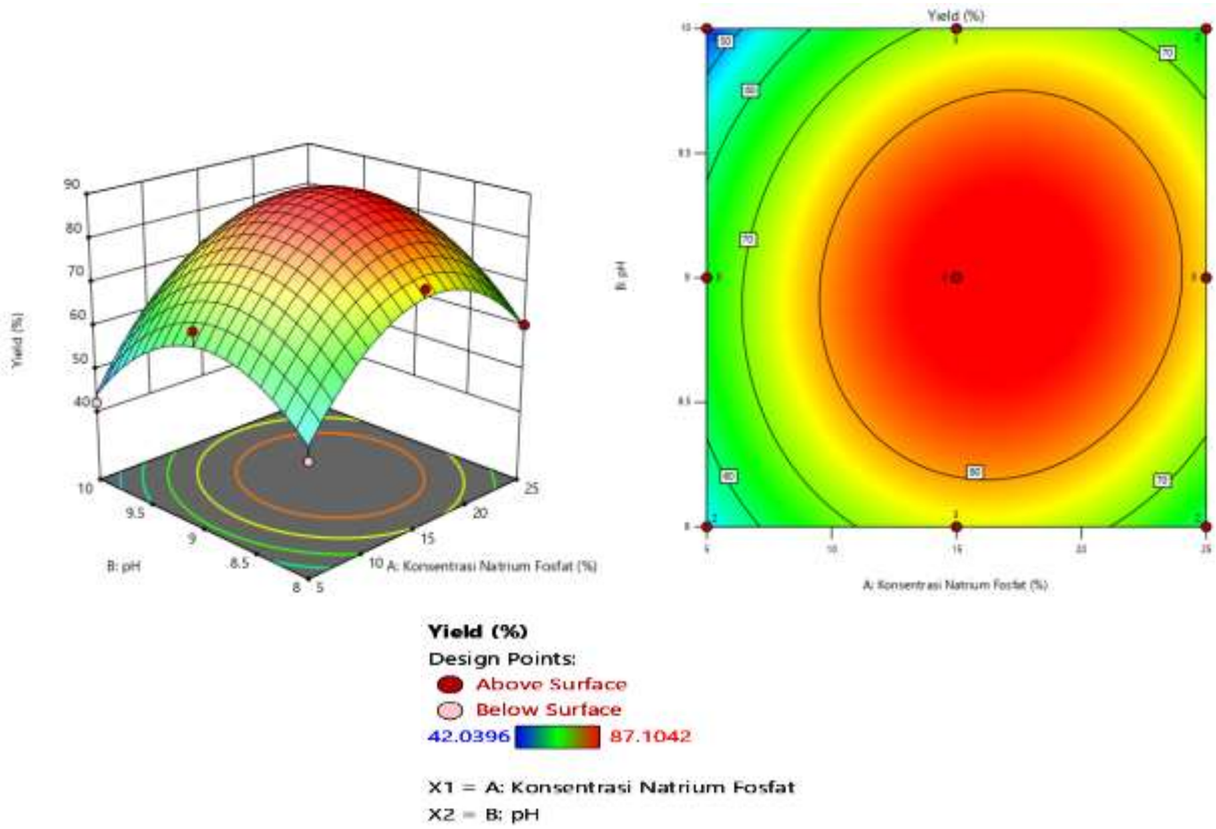

Figure 4. The 3D and Contour graphs of the effect of solution pH and sodium phosphate concentration on product yields

The optimal condition predicted by Design Expert Software was pH 8.83 and Na_3PO_4 concentration of 17.26%, resulting in a predicted purity of 77,324% and yield of 89,306%, with a desirability value of 1,00. This confirms the robustness and reliability of the model in identifying the best process parameters.

Table 5. Optimal solution based on RSM Design Expert 13

Na_3PO_4 Concentration (%)	pH	Mg_3PO_4 Content (%)	Yield	Desirability
17,264	8,830	77,324	89,306	1

Comparison with Previous Studies

The results of this study are consistent with previous research on magnesium precipitation from bittern using hydroxide or phosphate-based reagents. However, this study contributes further by integrating a statistical approach for process optimization, which enhances efficiency and reproducibility. Moreover, the use of Na_3PO_4 offers a cleaner reaction pathway and better control over product characteristics compared to multi-step extraction methods.

4. Conclusion

This study successfully demonstrated the conversion of magnesium from bittern into magnesium phosphate through a chemical precipitation process using sodium phosphate (Na_3PO_4). The results showed that pH and Na_3PO_4 concentration significantly affected the yield and purity of the product produced. The optimal condition was obtained at pH 9 with a Na_3PO_4 concentration of 15%, resulting in a maximum yield of 87.10% and product purity of 77.27%.

XRF analysis confirmed that the main components of the product were phosphate (68.5%) and magnesium (15%), with minor impurities such as calcium, bromine, and traces of heavy metals. This indicates that the product produced is of high purity and suitable for further application.

Further optimization using Response Surface Methodology (RSM) identified ideal conditions at pH 8.83 and Na_3PO_4 concentration of 17.26%, with a product yield of 89.31% and purity of 77.32%, and a desirability value of 1.000. These findings suggest that bittern, a by-product of salt production, has potential as a sustainable and economically viable feedstock for magnesium phosphate production, particularly in green fertilizer applications.

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