OPTIMIZING SYNTHESIS OF TiO_2 PIGMENT FROM TITANIUM SLAG USING HYDROTHERMAL ALKYLATION METHOD

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TÓM TẮT

TỐI ƯU HÓA QUY TRÌNH THU HỒI TiO_2 BẰNG PHƯƠNG PHÁP KIỀM HÓA THỦY NHIỆT

Khả năng kiểm soát khối lượng sản phẩm thu hồi cũng như cấu trúc tinh thể và hình thái học của hạt TiO_2 bằng cách điều chỉnh kích thước hạt nguyên liệu và các điều kiện của phản ứng thủy nhiệt chủ đề đang được quan tâm nhiều hiện nay. Xỉ titan là sản phẩm phụ của quá trình khai thác sắt từ quặng Ilmenit, có hàm lượng TiO_2 cao nên là vật liệu thích hợp để điều chế TiO_2. Nghiên cứu này đã thu hồi TiO_2 từ xỉ titan bằng phương pháp kiềm hóa thủy nhiệt. Hiệu quả của phương pháp này đã được đánh giá để tổng hợp TiO_2 từ xỉ titan. Các thí nghiệm với một yếu tố duy nhất đã được sử dụng để kiểm tra tác động của các thông số khác nhau đối với hàm lượng TiO_2 thu hồi như tỷ lệ rắn-lỏng (SLR), nồng độ NaOH và thời gian thủy nhiệt. Điều kiện tối ưu để thu hồi sản phẩm TiO_2 cao nhất được xác định tại nồng độ kiềm là 0,6 g/ml, thời gian phản ứng là 21 tiếng và nguyên liệu xỉ có kích thước trung bình 5,03 µm. Mô hình thiết kế Box-Behnken (BBD) được sử dụng để tối ưu hóa quy trình thu hồi. Bên cạnh đó, kết quả đo XRD được sử dụng để xác định cấu trúc tinh thể và thành phần pha của nguyên liệu xỉ và sản phẩm TiO_2, và kết quả đo XRF được dùng để xác định thành phần hóa học của chúng. Nghiên cứu này trình bày phương pháp kiềm hóa thủy nhiệt với các điều kiện tối để thu hồi TiO_2 từ xỉ titan một cách hiệu quả.

Key words: *TiO_2, rutile, titanium slag, hydrothermal, NaOH, Box-Behnken Design*

I. INTRODUCTION

Titanium dioxide (TiO_2) is an inorganic material in three crystalline phases: rutile, anatase, and brookite. TiO_2 is non-toxic, thermodynamically stable, inert, and less expensive than other materials [1]. These benefits make TiO_2 valuable for various industries, including the white pigment industry and photocatalysis applications [2]. The most widely used white pigment is the rutile phase of titanium dioxide. This phase has the highest refractive index of colorless and stable compounds. Therefore, TiO_2 is used in the commercial production of all kinds of paint, printing ink, plastics, paper, ceramics, food, and cosmetics [3]. TiO_2 is currently the most likely photocatalyst to be used in industrial-scale applications such as environmental purification, decomposition of carbonic acid gases, and solar cells [4].

The sulfate method was the first to produce the pigment TiO_2 commercially. It produces either rutile or anatase crystalline pigments [5]. However, the raw materials used in this method have a high iron concentration, producing vast amounts of waste iron sulfate and lower-quality products [6]. In the 1950s, Du Pont introduced the chloride method to the market, which has several advantages over the sulfate process in terms of energy, quality, and waste disposal [1]. The chloride process uses higher-grade rutile as the raw ingredient and can accommodate various feedstocks. Currently, the chloride process accounts for almost 60% of the 4,5 million tons of pigment produced worldwide [7]. The main drawback of this technology is the complexity of the process [8]. It is still necessary to develop alternative technologies to convert raw materials containing titanium into high-quality TiO_2.

Vietnam has significant potential for marine placers, with 2.8 million tons of proven primary and placer resources containing 30-70% $FeTiO_3$. Mineral sands, including ilmenite, zircon, monazite, and xenotime, are found along the 1,500 km coastline. TiO_2 is crucial for the painting, coatings, and construction industries, with the Vietnamese plastic industry's estimated consumption reaching 600,000 tons by 2023. However, domestic TiO_2 production is energy-intensive and faces high energy costs, affecting competitiveness [9]. Therefore, researching new production methods to reduce emissions, use cleaner technologies, and lower operational costs is essential.

Hydrothermal alkylation synthesis (HAS) is a technique that has shown potential for producing TiO_2 particles. The product's properties are determined by the formation mechanism and hydrothermal conditions used in this simple synthesis procedure [10]. This method has been applied in TiO_2 recovery studies, such as Synthesis of titanate nanofibers by a simple hydrothermal method from ilmenite mineral [11], A novel preparation of titanium dioxide from titanium slag [12]. In Vietnam, there are studies such as Synthesis of TiO_2 nanotubes by hydrothydrate method by Pham Nhu Phuong et al. [13], Preparement of nano titanium dioxide by hydrothermal method by Phan Minh Chau [14]. By changing the technological factors that control crystallinity, phase composition, and efficiency [15], it is possible to optimize the synthesis process. In this study, the effects of contributing factors such as titanium slag particle size, hydrothermal time, and NaOH concentration in solution on the efficiency of TiO_2 synthesis from titanium slag (the product of Binh Thuan ilmenite synthesis) by hydrothermal method, experiments were conducted. Response surface methodology (RSM) with Box-Behnken Design (BBD) models was used to optimize the hydrothermal conditions. Based on the results obtained, an efficient hydrothermal condition has been selected to boost the recovered TiO_2 mass (RTM) from titanium slag.

II. EXPERIMENT AND METHODOLOGY

Materials

Materials: Titanium slag (TS) was supplied by the Vietnam Institute for Titan Technology Science, located in Bac Binh, Binh Thuan, Vietnam, containing 92.01 % TiO_2. The titanium slag was ground into smaller particle sizes using a Planetary Mill (PULVERISETTE 5 Classic Line, Fritsch, Germany) for 10, 20, and 30 minutes to obtain three particle aggregates with average sizes of 5.78 µm, 5.03 µm and 3.53 µm, respectively.

Chemicals: Solid NaOH (96 %) and HCl (35.5 %) were purchased from Hoa Nam chemicals - laboratory equipment Company limited, Ho Chi Minh, Vietnam.

Produce

There are three stages involved in the synthesis of TiO_2 from TS. The first stage is the hydrothermal treatment. In this stage, solid NaOH is completely dissolved in distilled water to achieve concentrations of 0.4, 0.6, and 0.8 g/ml. Then, 25 g of titanium slag is added to the NaOH solution at a ratio of 1:10 g/ml. The mixture is stirred at 100 °C for one hour using a ceramic hotplate magnetic stirrer (IKA C-MAG HS7, Germany). Subsequently, the hydrothermal reaction takes place in a steel autoclave (200 ml) at 200 °C in an oven (DHG-9070, KeTon, China). The hydrothermal time varies from 18, 21, to 24 hours. The solid phase undergoes the hydrothermal reaction is vacuum filtered using a vacuum pump (VE115, China). The obtained solid is washed with distilled water to remove excess NaOH after the reaction and dissolved in a 20 % HCl solution at a SLR of 1:5 g/ml. The solution is maintained at 60 °C using a ceramic hotplate magnetic stirrer (IKA C-MAG HS7, Germany) for 1 hour and increased to 100 °C for the next 2 hours to perform hydrolysis. Finally, TiO2.nH2O settles at the bottom and is separated from the solution by vacuum filtration (VE115, China). The obtained solid product is calcined at 800°C for 1.5 hours to obtain high-purity TiO_2 powder (>95 % TiO_2).

Experimental design

RSM with BBD model was used so as to optimize the HAS process. The optimization was based on the results of a single-factor experiment where the independent variables were tested at three different levels (-1, 0, +1). Level 0 specifies the highest RTM value achieved under the HAS condition, levels -1 and +1 are used as boundary conditions. A second-degree polynomial regression model was employed to establish the relationship between the factors and the responses, described by Equation (1).

$$y = a_0 + \sum_{i=1}^{k} a_i x_i + \sum_{i=1}^{k} a_{ii} x_i^2 + \sum_{i=1<j}^{k} \sum_{j=1}^{k} a_{ij} x_i x_j \quad (1)$$

Where a_0 is the intercept, and a_i, a_{ii}, and a_{ij} symbolize linear, interactive, and quadratic coefficient, respectively.

Statistical analysis

The statistical analysis was conducted using ANOVA with a significance level of 5 %. Minitab 19 software (Minitab, Inc., Pennsylvania, USA) was used to carry out tests with multiple ranges. Graphs were created using the Origin Pro program (Origin Lab, Northampton, Massachusetts, USA). The BBD model was also determined using the Design-Expert software (Stat-Ease Inc., Minneapolis, Minnesota, USA).

II. RESULTS AND DISCUSSION

Effect of particle size

The study was conducted to investigate the impact of particle size on the efficiency of TiO_2 recovery from TS using the HAS process. The experiments were conducted at a reaction temperature of 200 °C, a SLR of 1/10 g/ml, NaOH concentration of 0.4 g/ml, and hydrothermal time of 18 hours. Three particle aggregates with average particle sizes of 5.78 µm, 5.03 µm, and 3.53 µm, respectively. The results, depicted in Fig. 1A, illustrate that the RTM increases as the particle size decreases, peaking in 5.03 µm.

Subsequently, the recovery mass decreases in 3.53 µm. The initial rise in mass could be attributed to the reduction in particle size, which enhances the specific surface area of the slag and its reactivity. This observation is consistent with findings by Tianyan Xue et al., who studied the decomposition kinetics of titanium slag in a sodium hydroxide system [16]. However, it may be problematic when particles are too small, leading to uneven dispersion. Small particles may agglomerate or disperse unevenly in the reaction medium, impacting efficiency [17]. Consequently, the study determined that an average particle size of 5.03 µm is suitable for recovering TiO_2 via hydrothermal alkalinization.

Effect of concentration NaOH

The study examined the impact of NaOH concentration on the efficiency of TiO_2 recovery. The experiment used a particle size of 5.03 µm with similar fixation conditions to investigate NaOH concentrations from 0.4 mg/l to 0.8 mg/l. As shown in Fig.1B, the results demonstrate that increasing the NaOH concentration from 0.4 to 0.6 g/ml enhances the TiO_2 recovery rate. This increase is due to the higher concentration of Na^+ ions, which promote more Ti to react. However, increases beyond 0.6 to 0.8 g/ml do not contribute to improved product recovery. This is because the solution's viscosity increases with the higher concentration of dissolved NaOH, hindering the movement and diffusion of Na^+ ions. As a result, the efficiency of TiO_2 recovery reaches a plateau or may even decline at excessively high NaOH concentrations. This aligns with the research of Herlina Rahim et al., who studied the effect of NaOH concentration on the silica leaching process from rice husk ash in South Sulawesi Province, Indonesia [18]. Therefore, NaOH concentration at 0.6 g/ml was relevant for process, ensuring the efficient recovery of TiO_2 from TS.

Effect of hydrothermal time

The study examined the effect of hydrothermal time on the recovery of TiO_2 from ilmenite slag in specific conditions. The reaction times studied were 18 hours, 21 hours, and 24 hours. The results showed that the volume of recovered products increased with increasing reaction time, reaching a peak at 21 hours before slightly declining when extended to 24 hours. This can be attributed to the initial rapid reactions that dissolve compounds like metal oxides and iron salts in the ore, followed by a slower process of breaking down stable Titanate structures. The reactions approach equilibrium after 21 hours, leading to a plateau in recovery efficiency. This is consistent with Dao Van Dung's discovery in the recovery of total oxides of rare earth elements from Quang Tri monazite ore using the alkaline method [19]. Therefore, the suitable decomposition time for compounding TiO_2 by the hydrothermal alkalinization method is 21 hours.

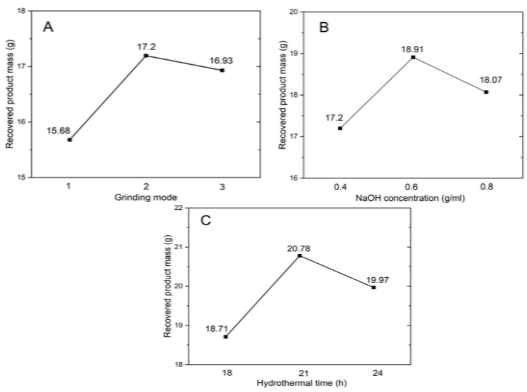

Figure 1. Recovered mass of TiO_2 powder with 3 factors. (A) 3 particle size 5.78, 5.03, and 3.53 µm. (B) NaOH concentration 0.4, 0.6, and 0.8 g/ml, (C) hydrothermal time 18h, 21h, and 24h

Optimization of the TiO_2 recovery process

The synthesis process involves 17 experiments using the BBD method. Three variables and three levels are used to evaluate the individual and interactive effects on performance, including particle size (x_1), NaOH concentration (x_2), and hydrothermal time (x_3).

Table 1. Results of experiments and predictions of RTM

No.	Factor x_1	Factor x_2	Factor x_3	RTM (g/g) Experimental Values
1	-1	-1	0	16.59
2	0	0	0	20.78
3	0	1	1	19.20
4	1	-1	0	19.99
5	-1	0	1	18.14
6	-1	0	-1	15.68
7	-1	1	0	19.84
8	1	0	1	18.02
9	1	1	0	19.02
10	1	0	-1	16.93
11	0	-1	-1	17.20
12	0	1	-1	18.07
13	0	-1	1	18.47
14	0	0	0	20.78
15	0	0	0	20.78
16	0	0	0	20.78
17	0	0	0	20.78

The results are presented in Table 1, which includes the predicted value of the RTM obtained from TS (Y). The equation representing the final quadratic polynomial model in the design is expressed as follows:

$$Y = 20.78 + 0.46x_1 + 0.49x_2 + 0.75x_3 - 1.05x_1x_2 - 0.34x_1x_3 - 1.48x_1^2 - 0.44x_2^2 - 2.10x_3^2 \quad (2)$$

ANOVA was used to evaluate the model presented in Table 2. The model showed a significant correlation between the RTM and the regression equation, which is quadratic in form. The F value and p-value of the model were 71.26 and <0.0001, respectively, indicating its significance. The coefficients in the equation were determined based on their respective p-values, and their importance was shown by $p < 0.05$. The polynomial equation (2) demonstrated a high correlation coefficient ($R^2 = 0.9892$), which exceeds the minimum R^2 threshold of 0.8 for a favorable model. It suggests a robust correlation between predicted and observed RTM values [20]. Furthermore, the coefficient of variation (CV) value was 1,39 %, less than 10 %. It indicates that the proposed model was highly accurate and reliable during testing [21].

Table 2. Analyze correlation coefficients of factors to RTM

	Coefficient Estimate	p-value
Intercept	20.78	< 0.0001
A-A	0.46	0.0016
B-B	0.49	< 0.0001
C-C	0.75	0.0012
AB	-1.05	< 0.0001
AC	-0.34	0.0345
BC	-0.03	0.8077
A^2	-1.48	< 0.0001
B^2	-0.44	0.0104
C^2	-2.10	< 0.0001
Degree of Freedom	16	
F-value	71.26	
C.V%	1.39	
R^2	0.9892	
$R^2_{Adjusted}$	0.9753	

Based on the regression analysis, RTM is influenced by the interactions of x_1x_2 and x_1x_3, which implies that particle size, NaOH concentration, and hydrothermal time play crucial roles in the TiO_2 recovery process. All variables in equation (2) demonstrate high significance ($p < 0.05$), with hydrothermal time exerting the most significant influence on recovery. The interactions among factors were visually presented using 3D response surface plots (Fig.2). The interaction between particle size and NaOH concentration affects process efficiency. At a particle size of 5.03 µm, the product volume decreases when the NaOH concentration reaches 0.6 g/ml. This might be due to potential accumulation or uneven dispersion of small-sized particles in the reaction medium, affecting reaction efficiency. Alternatively, the high NaOH concentration could have led to an excessively high basicity for subsequent hydrolysis, resulting in a slower process. For the hydrothermal time, increasing from 18 to 21 hours leads to an increase in TiO_2 content. The extended hydrothermal time allows the reactions to have more time to complete, resulting in more reactants being converted into the product. The diffusion process occurs more thoroughly, enabling the reactants to better interact and produce more product. However, when the time extends to 24 hours, the TiO_2 content begins to decrease. This is because prolonged reaction times can lead to the formation of new impurities or unwanted side reactions, which consume some of the reactants and reduce the amount of the main product.

The optimized recovery parameters achieved from the model were a particle size of 4.86 µm, NaOH concentration of 0.68 g/ml, and a time of 21.5 hours, resulting in an RTM objective function value of 20.98 g/g (Fig.3). To validate the obtained optimal values predicted by the model, the study conducted experiments according to the best-proposed conditions: a particle size of 5.03 µm, NaOH concentration of 0.6 g/ml, a hydrothermal time of 21 hours, a reaction temperature of 200 °C, and SLR of 1/10 g/ml followed by assessing the TiO_2 content in the slag. The results indicated an RTM of 20.83 g/g slag, which was in close agreement with the predicted outcome from the model.

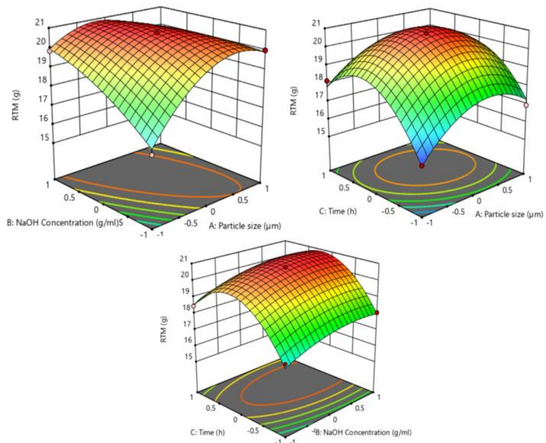

Figure 2. The 3D response surface plots expressing the significantly interactive effects of independent variables

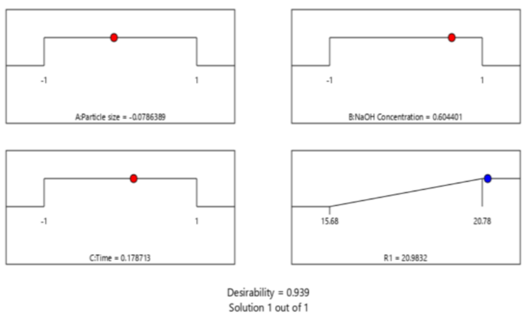

Figure 3. Expected function and optimal conditions for RTM

Phase structure analysis

Fig. 4 shows the phase compositions of the final product (95 % TiO_2) recovered from slag material 5.03 µm average particle size, 0.6 g/ml NaOH in the hydrothermal solution and 21-hour reaction time. The minerals of TiO_2 sample included a mixed phase of rutile represented by diffraction positions 27.9°, 36.5°, 39.6°, 41.6°, 48.3° 54.73°, 63.1°, 64.46°, 69.4° [22], anatase at 25.7°, 38.2°, 48.5°, 57°, 69.4°, 70.2° [23] and brookite observed at diffraction peaks 25.6°, 44.5°. Most peaks of the pattern represent for the rutile structure.

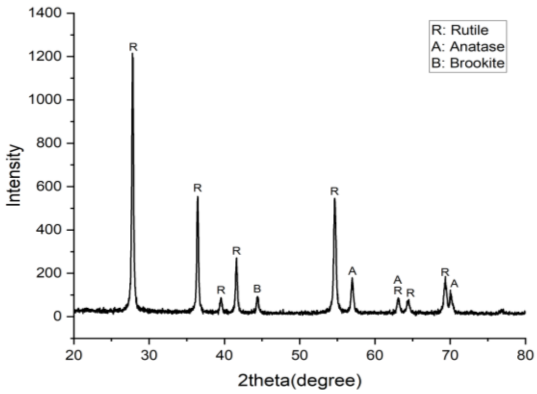

Figure 4. XRD patterns of high-grade TiO_2 powder

III. CONCLUSION

In this study, particle size, NaOH concentration, and hydrothermal time were identified as significant factors influencing the synthesis process of TiO_2 from titanium slag. Utilizing the Box-Behnken experimental design model in Design Expert software, the research determined the optimal conditions for TiO_2 recovery to be the use of 0.6 g/ml NaOH, a particle size of 5.03 µm, a reaction time of 21 hours, and SLR of 1/10 g/ml, resulting in a TiO_2 content of 20.83 g/g. Experimental verification yielded highly compatible results. Thus, the study successfully identified a process for TiO_2 recovery from titanium slag. It was observed that rutile exhibited the highest thermodynamic stability among the TiO_2 phases. During the hydrothermal reaction, with 0.6 g/ml NaOH in the solution, there was a full-phase transition of anatase and brookite to the rutile phase.

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