Optimization of the synthesis parameters and analysis of characteristics of 1,1-diamino-2,2-dinitroethylene

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ABSTRACT

2,2-Dinitroethene-1,1-diamine (FOX-7) is a low-sensitive explosive suitable for various energy-material applications. It can be synthesized based on the nitration and hydrolysis of heterocyclic precursors derived from 2-methylimidazole-4,5-dione (MID) or 2-methylpyrimidine-4,6-diol (MPD). However, more information about its optimal synthesis parameters during production from MPD as a starting material is needed. In this study, Taguchi's experimental design method was used to improve the yield of FOX-7. Verification of the results shows that the optimal synthesis parameters are as follows: the molar ratio of HNO_3/MPD is 8, the reaction time is 180 minutes, and the reaction temperature is 15°C; the maximum yield of FOX-7 can reach 79.14%. Furthermore, the synthesized FOX-7 was identified and characterized by nuclear magnetic resonance (NMR) spectroscopy analysis, Fourier transforms infrared spectroscopy (FTIR), Raman spectroscopy analysis, and powder X-ray diffraction (PXRD).

Keywords: FOX-7; 1,1-diamino-2,2-dinitroethylene; Synthesis; Optimization.

1. INTRODUCTION

In recent years, concurrent with the significant advancement of high-technology weaponry, the trend toward developing and utilizing safe munitions has garnered attention from numerous advanced nations [1]. Traditional explosive compounds such as TNT, RDX, and HMX are susceptible to external environmental stimuli and impacts. 1,1-Diamino-2,2-dinitroethylene (FOX-7) is a low-sensitivity explosive compound developed by the Swedish Defense Research Agency (FOI), first synthesized in 1998 [2-4], which has garnered significant interest among materials scientists [5-7]

In the past two decades, there has been a plethora of research studies and publications regarding the synthesis methods of FOX-7. For instance, Latypov et al. [4] synthesized FOX-7 via an intermediate compound, 2-(dinitromethylene)-4,5-imidazolidinedione, achieving a yield of 35%. Astrat'ev et al. [8] utilized 2-methylpyrimidine-4,6-dione (MPD) as the starting material to synthesize FOX-7 through the intermediate compound 2-dinitromethylene-5,5-dinitropyrimidine-4,6-dione, achieving a yield of up to 75%. However, this method is limited by expensive raw materials, significant heat release during nitration, and prolonged reaction times. Subsequently, Latypov et al. [9] also employed 2-methylpyrimidine-4,6-diol to synthesize FOX-7 via the intermediate compound 2-dinitromethylene-5,5-dinitropyrimidine-4,6-dione, with improvements in synthesis method resulting in a smoother reaction, higher product purity, and an overall yield of 75.6%.

The synthesis methods mentioned above all utilize expensive starting materials, resulting in high production costs for FOX-7. Consequently, despite its significant military and commercial potential, the high price has limited its utilization in both military and civilian sectors. Based on the previously published works on FOX-7 as outlined above, the author notes that to reduce production costs and enhance the synthesis yield of FOX-7, a two-stage approach is recommended: stage 1 involves synthesizing the precursor compound 2-methylpyrimidine-4,6-diol from

acetamidine hydrochloride and dimethyl malonate; stage 2 involves nitration and hydrolysis of 2-methylpyrimidine-4,6-diol. Notably, the second stage presents technological challenges with multiple reactions occurring during nitration and hydrolysis, influenced by various factors affecting the synthesis yield of FOX-7. These factors include the mole ratio of H_2SO_4/MPD, the mole ratio of HNO_3/MPD, reaction time, reaction temperature, and acid concentration. Based on publications [8, 10, 11], the optimal concentration of H_2SO_4 is determined to be 92%. The optimal mole ratio of H_2SO_4/MPD is 10:1. Furthermore, to align with industrial-scale FOX-7 synthesis conditions, the remaining factors are typically restricted within specific ranges: the mole ratio of HNO_3/MPD ranges from 4 to 8, reaction time ranges from 60 minutes to 180 minutes, and reaction temperature ranges from 5 °C to 15 °C. However, little information about its optimal synthesis parameters of nitration and hydrolysis stage is available. To identify the optimal parameters of these factors for the yield of FOX-7, the Taguchi method [12] is employed for experimental design, ensuring simplicity and effectiveness.

This study undertook the synthesis of FOX-7 using a two-stage method involving the synthesis of 2-methylpyrimidine-4,6-diol from acetamidine hydrochloride and dimethyl malonate, followed by nitration and hydrolysis reactions. Additionally, to optimize the nitration and hydrolysis process, the Taguchi experimental method was employed to select the reaction time, reaction temperature, and raw material/mol ratio of nitric acid. Three control factors were divided into three different levels, and nine experiments were planned using the $L_9(3^3)$ orthogonal array design. The structure and purity of FOX-7 were analyzed using FTIR infrared spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, Raman spectroscopy, and powder X-ray diffraction (PXRD). The morphology of FOX-7 crystals was evaluated by analyzing images acquired using an optical microscope.

2. MATERIALS AND METHODS

2.1. Materials

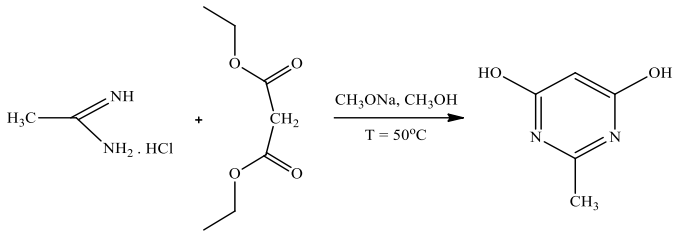
The reagents utilized in the synthesis of FOX-7 comprise acetamidine hydrochloride ($C_2H_6N_2$·HCl, 92%); dimethyl malonate ($C_5H_8O_4$, 98%); Sodium metal is preserved in n-hexane (Na, 99%); methanol (CH_3OH, 99.5%); hydrochloric acid (HCl, 37%); sulfuric acid (H_2SO_4, 98%); dimethyl sulfoxide DMSO ($(CH_3)_2SO$, 99.5%), sourced from Xilong Scientific Co., Ltd., China. Nitric acid 99% was provided by Z Co. Ltd., from Viet Nam. The purity of all chemicals is guaranteed by information from the supplier and can be used directly without purification. Concentrations of solvent and acid at different values are prepared and accurately titrated.

2.2. Methods

2.2.1. Synthesis of FOX-7

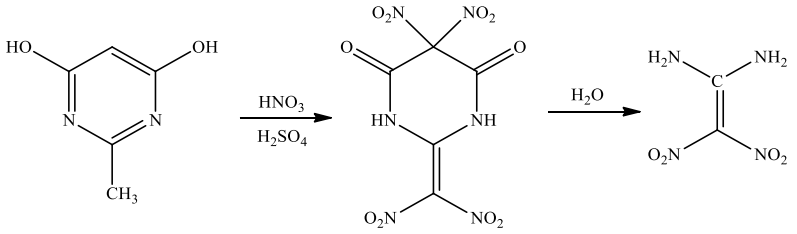
General caution. The mentioned compounds possess high energy properties, making them prone to combustion or detonation under certain conditions. Strict safety measures, such as wearing safety glasses, face shields, and flame-resistant clothing like leather coats, are essential to minimize risks during handling.

Add 300 ml of methanol into a 3-neck flask fitted with a stirring paddle and condenser. Set the circulating water bath temperature at 5 °C, stirring speed 300 rpm. Chop 11.5 g sodium (0.5 mol) (2x2 mm) and slowly add to the flask. Then, 18.9 g (0.2 mol) of acetamidine hydrochloride is added to the mixture, and after its dissolution, a solution of 32 g (0.2 mol) of dimethyl malonate in 40 mL of absolute methanol is added. The reaction mixture is heated to 50 °C and stirred at this temperature for 3 hours, then allowed to stand for 24 hours at room temperature. After standing, the mixture is neutralized with diluted hydrochloric acid to pH = 6. Then, 250 mL of distilled water is added and stirred into the flask for 1 hour. The precipitate is filtered and washed with water. The product is dried in a vacuum at 100 °C. The reaction yield achieves 95%.



Scheme 1. *Synthesis of 2-methylpyrimidine-4,6-diol (MPD).*

43 ml (ρ = 1.824 g.cm^{-3}) of 92% sulfuric acid (0.8 mol) are introduced into a three-neck flask outfitted with a proficient mechanical stirrer, thermometer, and dropping funnel. The acid is then heated, attaining a temperature range of 40-50 °C. Subsequently, 10 g (0.08 mol) of 2-methylpyrimidine-4,6-diol is incrementally added into the solution until complete dissolution is achieved. The resultant mixture is subsequently cooled to 5 °C, where 99% nitric acid is added. The reaction duration, temperature, and mass of 99% nitric acid were selected based on different reaction condition groups using the Taguchi experimental method, as illustrated in table 3. After completion of the reaction, ice is introduced into the flask, the quantity commensurate with the anticipated production of spent acid at a concentration of 25%. The resultant mixture is allowed to undergo hydrolysis of the tetranitro derivative over 24 hours. The ensuing 1,1-diamino-2,2-dinitroethylene product is subsequently subjected to filtration, followed by a washing step employing 40 ml of water. Finally, the washed product is dried at 100 °C in a vacuum.



Scheme 2. *Synthesis of FOX-7.*

Recrystallization of FOX-7 crystals was performed utilizing a DMSO ionic solvent as a co-solvent system (20:80 w/w). The crystallization process occurred at 60 ℃, where the remaining crystals were dissolved in methanol and then collected via filtration.

2.2.2. Experimental techniques

The PXRD experiments were conducted through a Bruker D8 Advance apparatus, and the structures were solved via direct methods with X'Pert HighScore Plus software, utilizing crystallographic data from CCDC 254069 and JCPDS No. 96-200-7995. These data are free from The Cambridge Crystallographic Data Centre, accessible via www.ccdc.cam.ac.uk.

FTIR Spectroscopy Perkin-Elmer Spectrum 400 spectrometer was used to identify the product through the FTIR spectrum. The wavenumber range used was 400 - 4000 cm$^{-1,}$ which is appropriate for most organic compounds. Using the FTIR spectrum made it possible to identify the main functional groups of the prepared materials.

Proton (^{1}H) and carbon-13 (^{13}C) nuclear magnetic resonance spectra were collected on a Bruker Avance 600 MHz spectrometer. The examined sample was dissolved in a suitable solvent (DMSO-d6), and then the sample was measured due to the magnetic field generated from the spinning charged nucleus.

The Raman spectra were measured using a LabRAM HR Evolution Raman spectrometer with the following parameters: the excitation source was a 532 nm green laser, power of laser 10-50 mW, spectral region 4000 - 400 cm^{-1}.

2.3. Design of the experiment conditions

This study used an $L_9(3^3)$ orthogonal array comprising three control factors and three levels, as previously described in the literature. These control factors encompassed the molar ratio of HNO_3 to MPD, reaction temperature, and reaction time, each delineated across three levels as outlined in table 1. These factors were then mapped onto the $L_9(3^3)$ orthogonal array, resulting in nine experimental configurations, as depicted in table 2. Additionally, the molar ratio of H_2SO_4 to MPD was constant at 10:1, and the concentrations of H_2SO_4 and HNO_3 were maintained at 92% and 99%, respectively.

Table 1. *The control factors and levels of the Taguchi experiments.*

Control factor	Level		
	1	2	3
A. Molar ratio of HNO_3 to MPD	4	6	8
B. Reaction time [min]	60	120	180
C. Reaction temperature [°C]	5	10	15

3. RESULTS AND DISCUSSION

3.1. Analysis and verification of the Taguchi experiments

The synthesis process of FOX-7 was conducted thrice under nine experimental condition groups planned using the Taguchi method, with the average experimental results presented in table 2. Among these, experimental condition group A9 (reaction time of 8 hours, reaction temperature of 10 °C, molar ratio of HNO_3 to MPD of 8) yielded the highest synthesis yield of FOX-7 at 78.92%.

Table 2. *Experimental results of Taguchi's orthogonal array.*

Exp. No.	Molar ratio of HNO_3 to MPD	Reaction time [min]	Reaction temperature [°C]	Yield of FOX-7 [%]
A1	4	60	5	57.96
A2	4	120	10	67.32
A3	4	180	15	72.53
A4	6	60	10	69.64
A5	6	120	15	73.13
A6	6	180	5	78.5
A7	8	60	15	71.34
A8	8	120	5	75.51
A9	8	180	10	78.92

The experimental data were converted into S/N values through Taguchi method analysis. The signal-to-noise (S/N) ratio indicates the impact of noise variables on the desired attributes. Broadly, three classifications of performance attributes are considered in S/N ratio analysis: "larger-the-better," "smaller-the-better," and "nominal-the-best." In this investigation, the yield of FOX-7 was selected as the target characteristic. Yield analysis employed the "larger-the-better" classification, wherein higher values denote higher yields. Table 3 delineates each factor's scope and significance ranking relative to the yield of FOX-7. The three controlling factors are the molar ratio of HNO_3/MPD (A), reaction time (B), and reaction temperature (C), which are 9.32%, 10.341%, and 1.68%, respectively. From there, it can be seen that the influence of each control factor on reaction yield is reaction time > molar ratio of HNO_3/MPD > reaction temperature. The trend of the impact of individual control factors on performance is shown in figure 1. The maximum yield of each control factor is the optimal condition, from which we have A3B3C3 as the optimal experimental condition. (the molar ratio of HNO_3/MPD is 8, the reaction time is 180 minutes, and the reaction temperature is 15 °C).

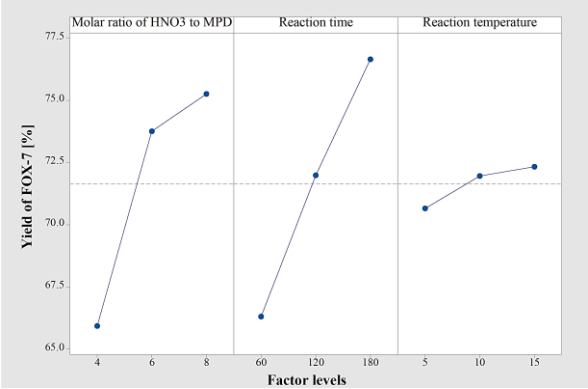


Figure 1. *The trend of parameter influence for the three factors on the yield of FOX-7.*

Table 3. *Range and contribution rank of each factor for the yield of FOX-7 (%).*

Level	Control factor		
	A. Molar ratio of HNO_3/MPD	B. Reaction time [min]	C. Reaction temperature [°C]
1	65.94	66.31	70.66
2	73.76	71.99	71.96
3	75.26	76.65	72.33
Range	9.32	10.34	1.68
Rank	2	1	3

Confirmation experiments must be conducted to validate the accuracy of the Taguchi experimental design scheme. Three parallel experiments are carried out under the optimal experimental combination conditions A3B3C3. The experimental results are showcased under these optimal parameter combination conditions, yielding an average synthesis of FOX-7 of 79.14%, surpassing that of the nine sets of experiments planned by the Taguchi method.

3.2. Structure determination

The synthesized FOX-7 was recrystallized in DMF and water solvents, exhibiting a bright yellow powder appearance, as shown in figure 2, with rod and cubic-shaped crystals, as depicted in figure 3. The FOX-7 product was subsequently analyzed using FTIR, NMR, Raman, and PXRD spectra for identification.

Figure 2. *Macroscopic morphology of FOX-7 crystals.*

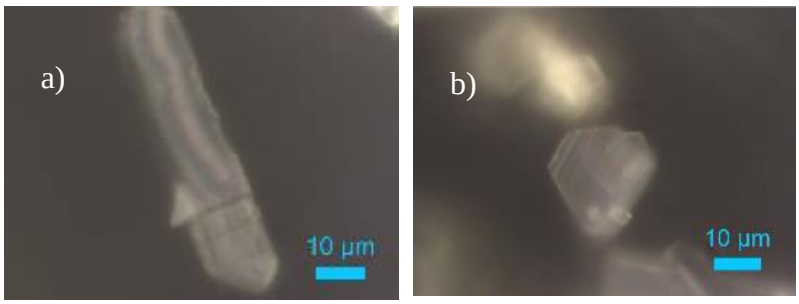


Figure 3. *Microscopic morphology of FOX-7 crystals: a) in DMF like rod-shaped, b) in water like cubic-shaped.*

3.2.1. Powder X-ray Diffraction Analysis

The FOX-7 crystals were analyzed through PXRD, and the structure of the synthesized FOX-

7 was determined using crystallographic data from CCDC 254069 and JCPDS No. 96-200-7995.

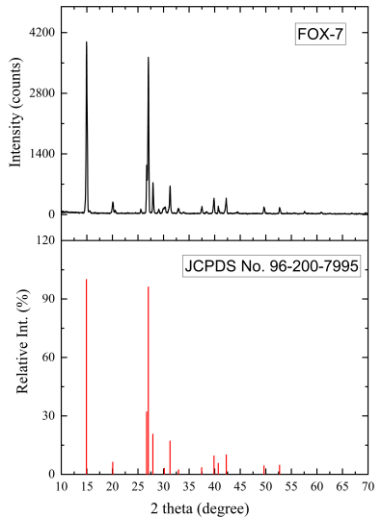


Figure 4. *PXRD data of synthesized FOX-7 in this study and data from JCPDS of FOX-7.*

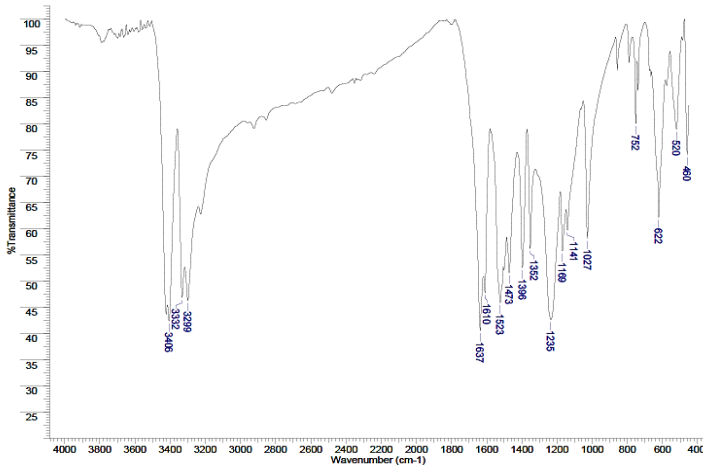


Figure 5. *FTIR spectrum of FOX-7.*

PXRD analysis was conducted to illustrate the crystal structure of recrystallized FOX-7 in DMSO/H2O (Fig. 4). The peak positions of diffraction peaks of recrystallized FOX-7 were matched perfectly with those of raw FOX-7 (CCDC 254069), indicating that the crystal phase of recrystallized FOX-7 was maintained to be α-FOX-7 (JCPDS No. 96-200-7995), as same as the raw material.

3.2.2. FTIR spectroscopic analysis

The FTIR spectrum of solid FOX-7 product (KBr disc) is illustrated in figure 5, featuring the following peaks: 3406 (-NH_2), 3332 (-NH_2), 3299 (-NH_2), 1637 (-NH_2), 1523 (-NO_2), 1473, 1396, 1352 (-NO_2), 1235, 1169, 1141, 1027, 752 (C=C), 622, 520, 460 cm^{-1}. The infrared spectrum of FOX-7 exhibits absorbance peaks within the 3299-3406 cm^{-1} range, indicative of the amino functionality, and 1352-1523 cm^{-1} range, characteristic of the nitro functionalities. After comparison with references [2, 13], it can be asserted that the synthesized product is FOX-7.

3.2.3. (^1H, ^{13}C)-NMR spectroscopic analysis

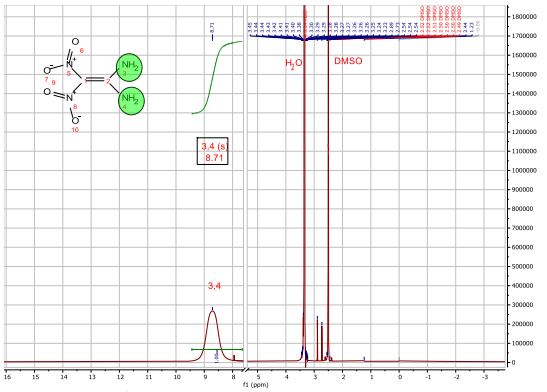


Figure 6. *^1H NMR spectrum of FOX-7.*

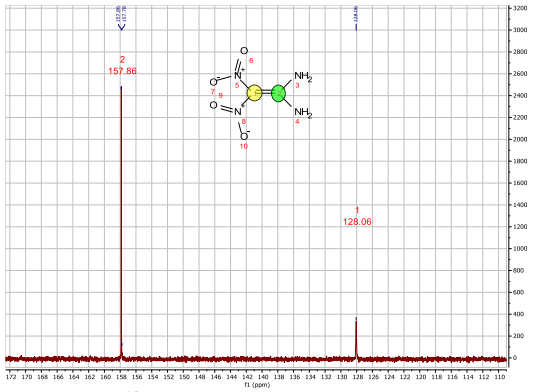


Figure 7. *^{13}C NMR spectrum of FOX-7.*

Dissolving the synthesized FOX-7 in DMSO-D6, nuclear magnetic resonance (NMR) spectroscopy (1H-NMR, 13C-NMR) was employed to analyze the product's structure. The ^1H-

NMR spectrum is depicted in figure 6. The chemical shift of its absorption peak is δ=8.71 ppm (s, 4H), consistent with the absorption peak position of H in the two -NH_2 groups of the FOX-7 molecule, in line with the literature [13] δ=8.76 ppm (s, 4H). Additionally, the ^{13}C-NMR spectrum is shown in figure 7, where the chemical shift δ=128.06 ppm corresponds to the chemical shift of C in the C-NH_2 bond, and the chemical shift at peak 157.86 ppm corresponds to the chemical shift of C in the C-NO_2 bond. These values match the corresponding literature, 129.42 ppm, and 159.03 ppm, respectively [13]. The NMR spectra (^{1}H-NMR, ^{13}C-NMR) obtained in this thesis indicate that the synthesized product is FOX-7.

3.2.4. Raman spectra

Figure 8 presents the Raman scattering spectra of the FOX-7 sample. The sample shows characteristic vibrational modes at 3418, 3328, 1601, 1519, 1456, 1337, 1202, 1162, 1139, 1060, 1022, 852, 786, 619, 478, 455 cm^{-1}, match the values specified in the literature [14]. The vibrational modes are mainly NH_2 twisting (619 cm^{-1}), rocking (1022–1456 cm^{-1}), scissoring (1519 cm^{-1}) and stretching (3328–3418 cm^{-1}), which is also mixed with NO_2 scissoring (852 cm^{-1}), C–C stretching (1139 cm^{-1}, 1456 cm^{-1}) and C–NO_2 stretching (1162 cm^{-1}, 1337 cm^{-1}).

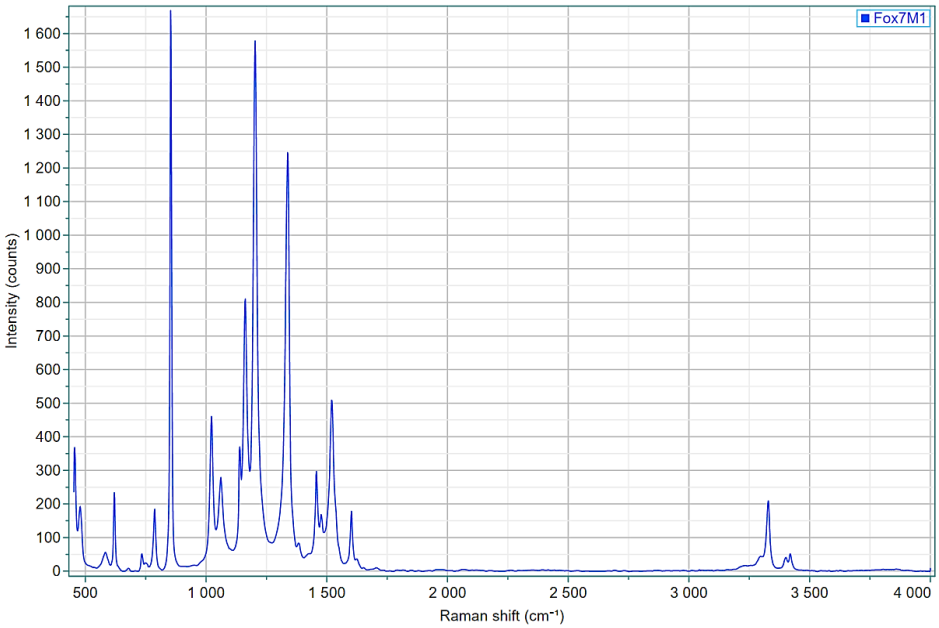


Figure 8. *Raman spectrum of FOX-7.*

4. CONCLUSIONS

In this study, FOX-7 was synthesized through 2 stages, including successfully using Taguchi's experimental design method in the nitrosation and hydrolysis stages to obtain the experimental conditions of the complex - optimal parameters to improve the yield of FOX-7 further. Under the condition that the molar ratio of H_2SO_4 and MPD is fixed at 10:1, the concentration of H_2SO_4 and HNO_3 acids is kept fixed at 92 and 99%. The optimal synthesis parameters are as follows: the molar ratio of HNO_3/MPD is 8, the reaction time is 180 minutes, the reaction temperature is 15 °C, stirring speed 300 rpm and the maximum yield of FOX-7 can reach 79.14%.

Several modern analytical methods, such as FTIR infrared spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, Raman spectroscopy, and powder X-ray diffraction (PXRD), were used to identify the synthesized FOX-7. The results of the above measurements are consistent with the values in the cited reference sources.

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TÓM TẮT

Tối ưu hóa các thông số tổng hợp và phân tích một số đặc trưng của 1,1-diamino-2,2-dinitroethylene

2,2-Dinitroethene-1,1-diamine (FOX-7) là chất nổ kém nhạy thích hợp cho các ứng dụng trong vật liệu năng lượng. FOX-7 có thể được tổng hợp bằng cách nitro hóa và thủy phân các tiền chất dị vòng từ 2-methylimidazole-4,5-dione (MID) hoặc 2-methylpyrimidine-4,6-diol (MPD). Tuy nhiên, có rất ít thông tin về các thông số tổng hợp tối ưu của FOX-7 trong quá trình sản xuất từ MPD. Trong nghiên cứu này, phương pháp thiết kế thử nghiệm của Taguchi đã được sử dụng để cải thiện hơn nữa hiệu suất của FOX-7. Kiểm chứng kết quả cho thấy các thông số tổng hợp tối ưu như sau: tỷ lệ mol HNO_3/MPD là 8, thời gian phản ứng là 180 phút và nhiệt độ phản ứng là 15 °C; hiệu suất thu được của FOX-7 có thể đạt 79,14%. Ngoài ra, FOX-7 được xác định và phân tích bằng quang phổ cộng hưởng từ hạt nhân (NMR), quang phổ hồng ngoại (FTIR), phổ Raman và nhiễu xạ tia X (PXRD).

Từ khoá: FOX-7; 1,1-diamino-2,2-dinitroethylene; Tổng hợp; Tối ưu hóa.