STUDY ON APPLICATION OF $BiFeO_3$ IN TREATING METHYLENE BLUE IN TEXTILE DYEING WASTEWATER

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Abstract: *This study presents the process of synthesizing $BiFeO_3$ by the Gel – Polymer combustion method under optimal condition, selected through the investigation of influencing factors and the characteristic of materials, including the Gel formation temperature (80°C), the molar ratio of Bi/Fe (1/1), the molar ratio of the mixture metal/PVA (1/3), pH=1, and the sample is heated at 500°C for 2 hours. Application of $BiFeO_3$ on removal 100ml of textile dyeing wastewater at concentration 5ppm methylene blue shows relatively good results y at different dilution conditions (f = 2, 5, 10) is 49-65% removal efficiency. The highest efficiency has been obtained in condition the sample was diluted 10 times in 120 minutes contact time under ultraviolet light (wavelength λ = 285nm).*

Keywords: *Methylene blue, modified materials, textile dyeing, $BiFeO_3$.*

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1. INTRODUCTION

The textile dyeing industry is considered one of the industries with the largest amount of wastewater. The massive development of the textile dyeing industry has been causing serious impacts on the environment. Textile dyeing industry wastewater contains a variety of aromatic compounds that are persistent in the environment. Moreover, in an anaerobic environment, some dyes will be reduced to form aromatic cyclic amines, which are toxic substances that cause cancer and mutations in both humans and animals. Methylene blue is a dark green heterocyclic aromatic compound that was synthesized more than 120 years ago and is widely used in the textile industry. Methylene blue in textile dyeing wastewater is very difficult to be decomposed; it not only affects the beauty of the environment but also affects the production, daily life, and health of humans, animals, and plants. In order to contribute to finding an effective method for treating methylene blue in textile dyeing wastewater, based on the knowledge from previous successful studies on the application of modified materials in textile dyeing wastewater pollution treatment. This study conducted the synthesis of $BiFeO_3$ materials for methylene blue treatment in textile dyeing wastewater.

2. MATERIALS AND METHODS

2.1. Object and scope

- Synthesis of BiFeO3 materials by gel-polymer combustion method
- Application of treating textile dyeing wastewater containing methylene blue in the laboratory.

2.2. Methodology

2.2.1. Methods of sampling and preservation of samples

Methods of sampling and preservation of samples following QCVN 40:2011/BTNMT: Regulation on the technical process of industrial wastewater monitoring. National standard TCVN 6663-32008 on Water quality - Sampling - Part 3 Guidelines for storage and handling of samples.

2.2.2. Materials synthesis method

a) The process of synthesizing materials is carried out according to the following diagram:

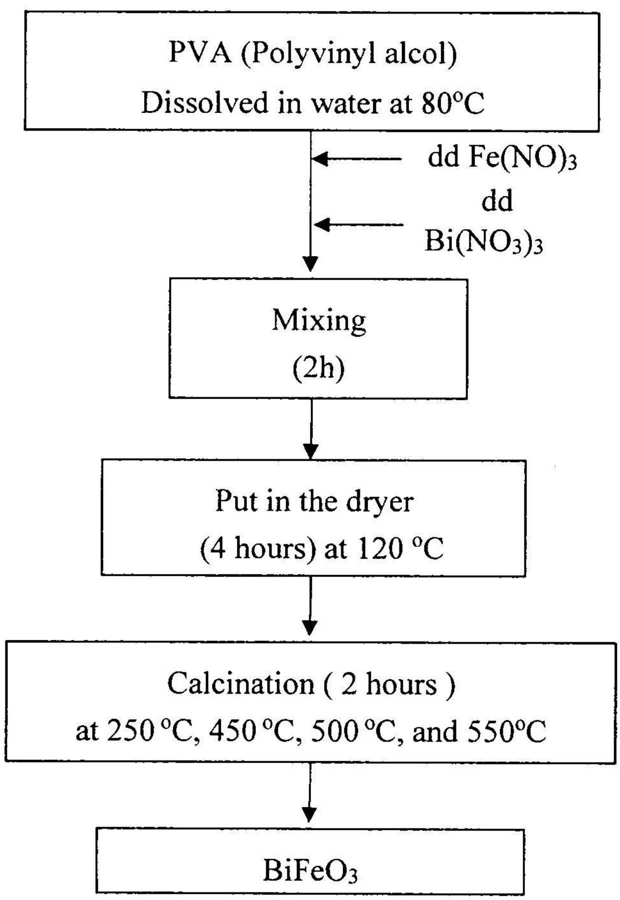


Figure 1. Schematic diagram of BiFeO3 synthesis by gel-polymer combustion method

b) The process of investigating factors affecting the synthesis of materials:

Surveyed factors: calcination temperature and Bi/Fe ratio

- The calcination temperature affects the phase formation of $BiFeO_3$, and the samples are heated at the following temperatures: 250 °C, 450 °C, 500 °C, and 550°C in the same period (2 hours). Then, the phase composition was analyzed at different temperatures on the X-ray diffraction pattern recorded on the Siemens D5000 machine.

- Metal Ratio: studied at the following ratio: 5/1, 3/1, 1/1, 1/3, 1/5, respectively. Subsequently, the phase composition was analyzed at different temperatures on the X-ray diffraction pattern recorded on the Siemens D5000 machine.

Table 1. Chemicals to study the effect of metal molar ratio

Bi/Fe ratio	**5/1**	**3/1**	**1/1**	**1/3**	**1/5**
$V_{Bi(NO_3)_3}$**(10g/l)**	10,45 ml	6,27 ml	20,9 ml	2,09 ml	2,09 ml
$V_{Fe(NO_3)_3}$**(10g/l)**	0,56 ml	0,56 ml	5,6 ml	1,68 ml	2,8 ml
m_{PVA}	0,079 g	0,053 g	0,026g	0,053 g	0,079 g
pH = 1	Adjusting by HNO_3				

c) Investigation of material morphological and structure

- Scanning electron microscopy (SEM): Using magnetic diffraction electron microscope on Hitachi S-4800 (Japan).

- Ronghen diffraction method (X-Ray): Using Siemens D5000 to record X-ray diffraction.

2.2.3. Method for determining methylene blue

- Methylene blue content was determined by the colorimetric method at wavelength λ = 660 nm. Methylene blue standard series were diluted with increasing concentrations from the working solution at 100ppm.

Table 2. Chemicals and procedure for methylene blue calibration

No.	**0**	**1**	**2**	**3**	**4**	**5**	**6**	**7**
$V_{xanhmetylen}$	0	1	1,5	2	2,5	3	3,5	4
C (ppm)	0	1	1,5	2	2,5	3	3,5	4
Leveled by distilled water								
Stabilized for 15 min, measured Abs at wavelength λ = 660nm								

From the known concentration of the standard series and the corresponding Abs value measured, we can establish the equation in the form y = ax + b

In which, y: Optical absorbance; x: Methylene blue concentration (ppm)

2.2.4. Process of applying methylene blue treatment

0.025g of $BiFeO_3$ synthesized under optimal conditions was added to the environmental or standard sample. Methylene blue was decomposed in 30, 45, 60, 90, and 120 minutes under ultraviolet light with wavelength $\lambda = 285$ nm (the whole reaction system is placed on a magnetic stirrer). After 30 minutes, the light and stirrer were stopped. 5ml of material was taken into the centrifuge tube and centrifuged for 10 min at 4000 rpm. Then, the sample was transferred to a quartz cell photometrically and measured at wavelength $\lambda = 660$nm.

The methylene blue degradation efficiency was calculated using the formula:

$$H(\%) = \frac{Co-Ct}{Co} x\ 100$$

Where: C_o: Initial methylene blue concentration (ppm)

C_t: Concentration of methylene blue at time t (ppm)

2.3. Results

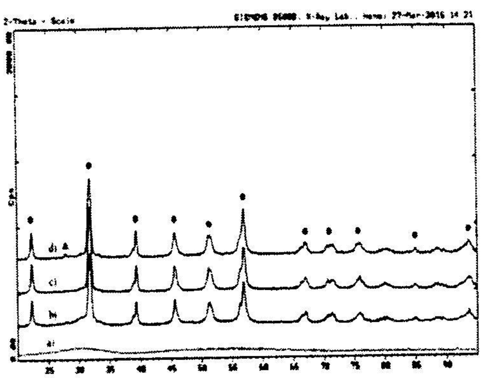
2.3.1. Survey results of influencing factors

2.3.1.1. Effect of heating temperature

The results of the phase composition of the heated samples at different temperatures were shown in Figure 2. According to the XRD Diagram, the heat supplied to the BFO material at 250°C is not enough to form crystals $BiFeO_3$. At 450°C, the crystalline phase of $BiFeO_3$ has been formed. Continuing to raise the temperature to 500°C, the crystalline phase was unique, unchanged, shown more clearly, and crystallized better. When the temperature was raised to 550°C, a small fraction of the β-Bi_2O_3 phase appeared because the perovskite structure was broken in the air. Therefore, the calcination temperature at 500°C was the optimal and selected temperature for the synthesis of materials.

2.3.1.2. Effect of metal ratio

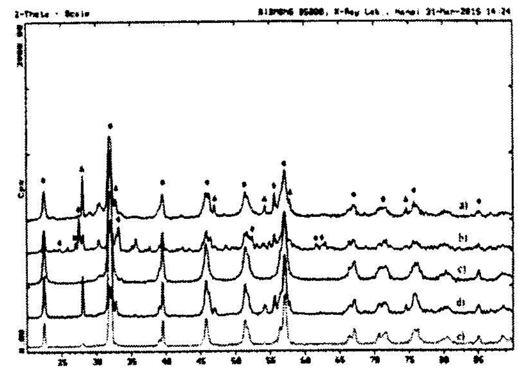
The results of phase composition analysis of the samples at different Bi/Fe ratios were shown in Figure 3. XRD diagram showed that at molar ratios 5/1, 3/1, 1/3, 1/5 in addition to the $BiFeO_3$ perovskite phase, there were additional phases of β-Bi_2O_3, $Bi_{36}Fe_2O_{57}$, α-Bi_2O_3 due to the lack or excess of iron and bismuth, so it could not enter the bond to form the $BiFeO_3$ perovskite phase. To make a single-phase of $BiFeO_3$, the Bi/Fe ratio = 1/1 was optimal.



●$BiFeO_3$ ▲β-Bi_2O_3 ♦$Bi_{36}Fe_2O_{57}$ ▪α-Bi_2O_3

Figure 2. XRD pattern of samples calcined at different temperatures:

a- 250°C. b-450°C c, 500 °C d, 550 °C



●$BiFeO_3$ ▲β-Bi_2O_3 ♦$Bi_{36}Fe_2O_{57}$ ▪α-Bi_2O_3

Figure 3. XRD pattern of samples with different Bi/Fe ratios.

a-5/1; b-3/1; c-1/1; d-1/3; e-1/5

2.3.2. Results of the investigation of the morphology and structure of materials

The sample materials were fabricated under optimal conditions: the gel-forming temperature was 80°C, the Bi/Fe ratio was 1/1, the molar ratio of the mixture metal/PVA=1/3, pH=1, samples were calcined at 500°C for 2 hours. Phase compositions were determined on Siemens D 5000 and micromorphology was determined on S 4800 machines.

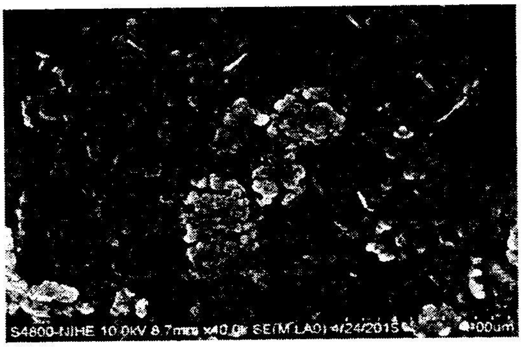


Figure 4. SEM pic of $BiFeO_3$ synthesized under optimal conditions.

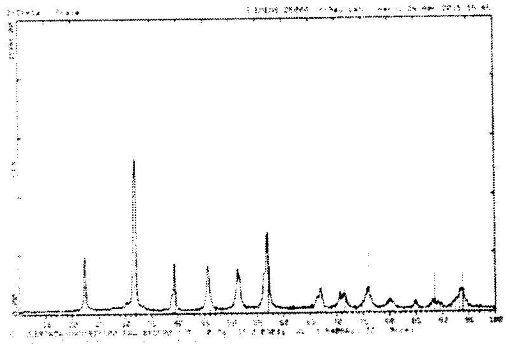


Figure 5. X-ray diffraction pattern of $BiFeO_3$ samples synthesized at optimal conditions

Based on the X-ray diffraction pattern (Figure 5) and SEM image (Figure 4), it showed that the synthesized sample under optimal conditions was a single-phase $BiFeO_3$ with a relatively uniform perovskite structure, particle size < 50 nm.

2.3.3. Results of photocatalytic activity of BFO on the degradation of methylene blue

Under the effect of ultraviolet light with wavelength $\lambda = 285$ nm, the BFO material was activated and became an active catalyst promoting the decomposition of methylene blue according to the reaction equation:

$$C_{16}H_{18}N_3SCl + 51/2\ O2 \rightarrow HCl + H_2SO_4 + 3HNO_3 + 16\ CO_2 + 6\ H_2O$$

2.3.3.1. Preparation of methylene blue standard curve

The optical measurement results (Abs) of the standard sample series were as follows

Table 4. *Optical measurement results of the standard series*

No.	**0**	**1**	**2**	**3**	**4**	**5**	**6**	**7**
C (ppm)	0	0,5	1	1,5	2	2,5	3	3,5
Abs	0,074	0,165	0,253	0,337	0,435	0,525	0,609	0,697

Construction of a methylene blue standard curve with the standard curve equation:

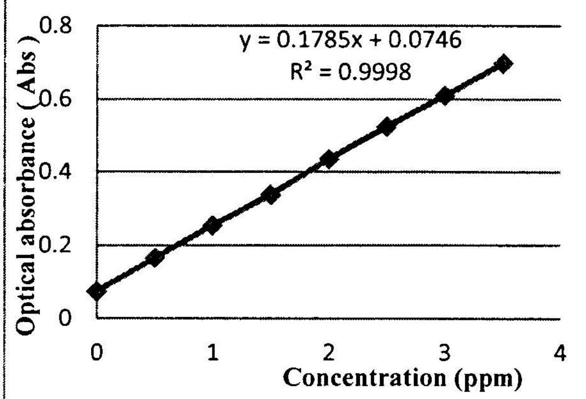
$$y = 0,178x + 0,074\ (r^2 = 0,999)$$

Where:

y: Optical absorbance (Abs)

x: Methylene blue concentration (ppm)

Figure 6. Methylene blue standard curve



2.3.3.2. Application of treating methylene blue in standard samples

The experiment was performed with 100 ml of standard methylene blue solution with a concentration of 5 ppm. Results showed that methylene blue was almost completely decomposed in 60 minutes.

Table 5. Results on photocatalysis degradation of methylene blue

Degradation time T (min)	**Methylene blue concentration C (ppm)**	**Treating efficiency H (%)**
30	4,980	80,07
45	1,880	95,25
60	0,310	98,76
90	0,125	99,05
120	0,125	99,05

2.3.3.3. Application of treating methylene blue in environmental samples

a, Determination of methylene blue content in environmental samples

After the sample was collected, the input content was analyzed.

Table 6. Methylene blue content in the input sample

No.	**Diluted 10 times**	**Diluted 5 times**	**Diluted 2 times**
Abs	0,563	1,082	2,635
$y = 0{,}178x + 0{,}074$ ($r^2 = 0{,}999$) Where: y: Optical absorbance x: Methylene blue concentration (ppm)			
C (ppm)	2,747	5,663	14,388
C environmental sample = 28,19 ppm			

b, Treatment of methylene blue in the environment with $BiFeO_3$

100ml of environmental samples were performed at different dilutions: 2, 5 and 10 times. The results on the degradation of methylene blue in environmental samples by photocatalysis over periods were shown in Table 7.

Table 7. Results on photocatalysis degradation of methylene blue in environmental samples

Time (min)	**Diluted 2 times (MT2)**			**Diluted 5 times (MT5)**			**Diluted 10 times (MT10)**		
	Abs	**C (ppm)**	**H (%)**	**Abs**	**C (ppm)**	**H (%)**	**Abs**	**C (ppm)**	**H (%)**
30	1,743	9,376	34,61	0,701	3,522	37,79	0,382	1,730	37,01
45	1,436	7,652	46,63	0,582	2,854	49,60	2,289	1,208	56,03
60	1,403	7,466	47,93	0,518	2,494	55,95	0,284	1,180	61,14
90	1,362	7,236	49,53	0,517	2,489	56,04	0,246	0,966	64,82
120	1,360	7,225	49,61	0,517	2,489	56,04	2,245	0,961	65,03

At all three dilutions, the strongest treatment occurred at the first 30 min and gradually decreased at subsequent time intervals. After 90 minutes, the photocatalytic ability with the environmental samples increased insignificantly.

Compared with the results from the standard sample treatment, the material content = 0.025g $BiFeO_3$ had a treating efficiency of more than 98% for the standard sample with a methylene blue concentration of 5ppm over a period of 60 minutes. The difference of this result could be due to:

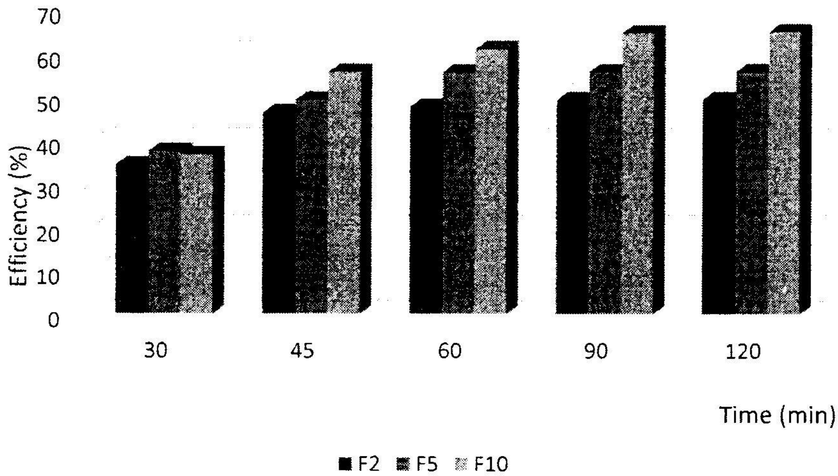


Figure 7. Graph showing the time dependence of the methylene blue degradation efficiency for the 3 dilutions of 2, 5, 10 times.

- The interfering factors affecting the optical measurement process have not been removed from all the environmental samples.

- In the environmental samples, there were many types of dyes, which affected the photocatalytic ability of the material.

3. CONCLUSION

Among all material synthesis methods, the selection of the Gel - Polymer combustion method to synthesize $BiFeO_3$ was very appropriate and effective. During the synthesis process, the optimal conditions to synthesize $BiFeO_3$ have been studied and found to be: the Bi/Fe ratio was 1/1, the sample heating temperature was 500°C. $BiFeO_3$ synthesized by the Gel - Polymer combustion method under optimal synthesis conditions has given certain efficiency. The material was synthesized in a single phase, particle size <50 nm. The photocatalytic properties of the material with standard methylene blue were very good. The decomposition efficiency H was more than 99%. Initial assessment showed that the ability to treat methylene blue by the photocatalytic properties of the material in textile dyeing wastewater had a certain efficiency (H = 49-65%), but the efficiency was not high.

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NGHIÊN CỨU ỨNG DỤNG XỬ LÝ XANH METYLEN TRONG NƯỚC THẢI DỆT NHUỘM BẰNG VẬT LIỆU $BiFeO_3$

Tóm tắt: *Nghiên cứu trình bày quy trình tổng hợp vật liệu $BiFeO_3$ bằng phương pháp đốt cháy Gel – Polyme trong điều kiện tối ưu được lựa chọn qua quá trình khảo sát các yếu tố ảnh hưởng và cấu trúc, hình thái vật liệu như: nhiệt độ tạo Gel ở 80^oC, tỷ lệ mol kim loại Bi/Fe là 1/1, tỷ lệ mol hỗn hợp kim loại/PVA=1/3, pH=1, nung mẫu ở 500^oC trong 2 giờ. Kết quả ứng dụng vật liệu $BiFeO_3$ xử lý 100ml nước thải dệt nhuộm có chứa dung dịch xanh metylen nồng độ 5ppm cho kết quả tương đối tốt với hiệu suất xử lý mẫu ở các điều kiện pha loãng khác nhau (f = 2, 5, 10) là 49 – 65%. Hiệu suất xử lý cao nhất ở điều kiệnpha loãng 10 lần với thời gian 120 phút phân hủy dưới ánh sáng UV có bước sóng λ = 285nm.*

Từ khoá: *Methylene xanh, xử lí vật liệu, dệt nhuộm, $BiFeO_3$.*