

## **MODIFICATION OF TITANIUM DIOXIDE NANOMATERIALS BY SULFUR FOR PHOTOCATALYTIC DEGRADATION OF METHYLENE BLUE EVEN UNDER VISIBLE LIGHT**

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### **ABSTRACT**

This paper presents a study on preparation of sulfur doped titanium dioxide using potassium fluorotitanate and sodium sulfate as precursors. The obtained results indicated that the doped TiO<sub>2</sub> exhibited very high photocatalytic activity for degradation of methylene blue even under visible light. The increasing in the added sulfur amounts led to significantly increase in the degradation of methylene blue. When the S/TiO<sub>2</sub> mole ratios increased from 10 to 25%, the degradation of methylene blue under compact light increased from 30.87% to 67.06%, respectively.

*Keywords:* potassium fluorotitanate, titanium dioxide, sulfur, photocatalyst, visible light.

### **1. INTRODUCTION**

Titanium dioxide (TiO<sub>2</sub>) could mineralize various toxic organic compounds into harmless inorganic substances such as CO<sub>2</sub> and H<sub>2</sub>O. However, TiO<sub>2</sub> could be only activated by UV radiation because of its wide band gap energy ( $E_{bg} = 3.2$  eV), which is equivalent to radiation of wavelength less than or equal to 389 nm [1]. The use of the UV irradiation as the excitation source accompanies by safety issues and high energy consumption. Solar light is a natural radiation source, however, there is only approximately 7 % of the solar radiation lies in the UV region leading to the small use of TiO<sub>2</sub> under solar radiation. Therefore, enhancing optical absorption of TiO<sub>2</sub> into visible region will open a new era to apply the semiconductor for treatment of environmental pollutants.

There are numerous studies have been conducted to improve photocatalytic efficiency of the TiO<sub>2</sub> [2 - 7]. They can be classified in two major methods including surface modification and band gap modification. Most of the reported studies concentrated on modification of titanium

dioxide, using transition metals (Fe, Cr, Ni, Ag, Cu) and non-metals such as N, S or C, to improve activity of the photocatalyst to effective use even under visible light.

In addition,  $\text{TiO}_2$  is usually synthesized from alkoxides, titanium salts etc, leading to increase in cost of the synthesized materials. Therefore, the first aim of the study was to use potassium fluorotitanate, prepared from Binh Dinh ilmenite ore to synthesize  $\text{TiO}_2$  to decrease cost of the synthesized  $\text{TiO}_2$ . Then, the synthesized  $\text{TiO}_2$  was modified by sulfur to enhance its photocatalytic activity for degradation of methylene blue even under visible light.

## EXPERIMENT

### 2.1. Materials and analysis

All the chemical reagents of analytical grade and deionized water were used throughout. The ilmenite used in the present study was supplied Binh Dinh Minerals Joint Stock Company, Vietnam.

Phase composition of  $\text{TiO}_2$  was determined by X-ray diffraction (XRD) method (D8-Advance 5005). Material surfaces were characterized by scanning electronic microscopy (SEM) (JEOL JSM-6500F). The specific surface area was measured by Brunauer–Emmett–Teller (BET)  $\text{N}_2$  adsorption methods (Micromeritics Tristar 300). Light absorption capability was evaluated by UV–vis absorption spectroscopy (3101PC Shimadzu). Chemical composition of catalysts were revealed by Energy-dispersive X-ray spectroscopy (EDS) (Kratos Axis ULTRA). Methylene blue concentration was determined by spectrometric method at 664 nm [8].

### 2.2. Synthesis of S-TiO<sub>2</sub>

The process of S-TiO<sub>2</sub> synthesis from Binh Dinh ilmenite ore was shown in Figure 1.

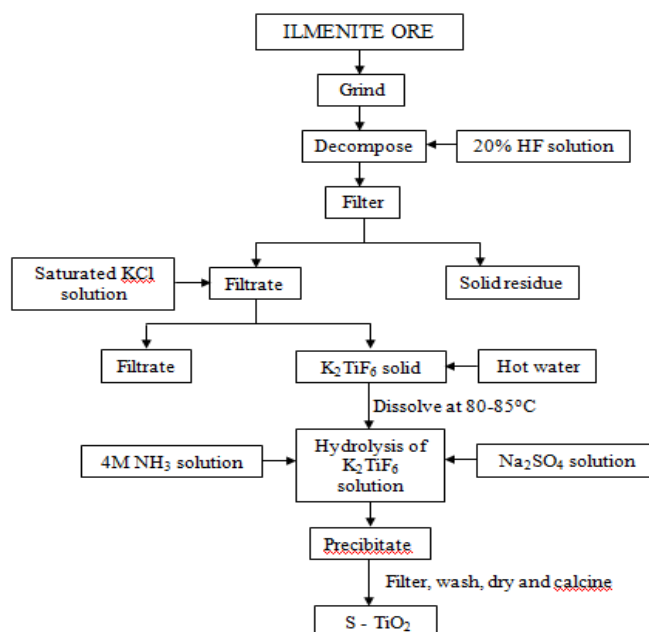


Figure 1. The process of S-TiO<sub>2</sub> synthesis from Binh Dinh ilmenite ore.

S-TiO<sub>2</sub> (TS550) catalyst was synthesized under conditions different ratio mol S/TiO<sub>2</sub>, hydrolysis time 2 hours and calcination temperature 550°C for 5 hours. TiO<sub>2</sub> (T550) catalyst was synthesized in the same conditions without using Na<sub>2</sub>SO<sub>4</sub> solution.

### 2.3. Methylene blue degradation experimental set-up

A methylene blue stock solution of 1 g/L has been prepared by taking 1 g of methylene blue and dissolving it in deionized water up to 1000 mL. Use it to prepare 1000 mL of 10 mg/L methylene blue solution. Take 600 mL of 10 mg/L methylene blue solution in 1000 mL beaker. For each test, 0.20 g catalyst was added. Before reaction, the solution was stirred in the dark for 2 hours to adsorption balance of the reactant on the surface of catalyst. Light source in this experiment was natural solar light (from 08.00 am to 11.00 am in summer, the days had the light intensity to be equivalent) and the light of compact lamp (60 W). After the reaction time was 3 hours, 2 mL samples were taken and centrifuged at 6000 rpm for 20 min. Then, 1.5 mL of the supernatant was then put in a disposable cuvette and analyzed using a UV-vis spectrophotometer (UV 1800, Shimadzu).

## 3. RESULTS AND DISCUSSION

### 3.1. Characterization of TiO<sub>2</sub> and S-TiO<sub>2</sub> materials

The XRD patterns of the synthesized TS550 and T550 were shown in Figure 2.

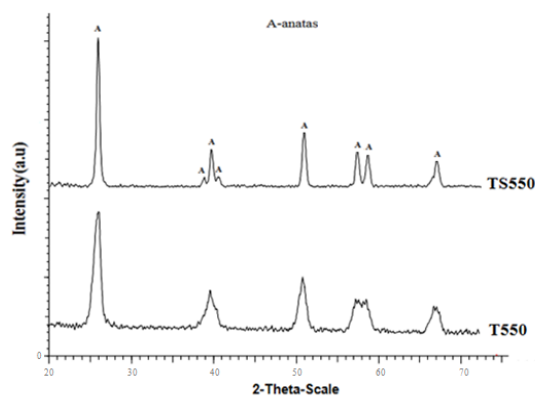


Figure 2. XRD pattern of TS550 and T550.

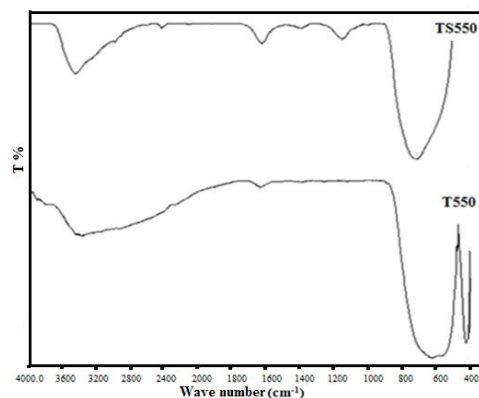


Figure 3. IR spectra of TS550 and T550.

The obtained results indicate that peaks at 25.26°; 37.78°; 38.56° corresponding to component of anatase phase. However, the intensity of peaks in anatase phase of TS550 sample is higher than those of the T550 sample. The results show that TS550 material was synthesized from Binh Dinh ilmenite ore only gives anatase form at 550 °C.

TS550 and T550 materials were characterized by IR spectroscopy. The results were shown in Fig. 3. It can be seen that IR spectrum of TS550 sample in Figure 3 shows bands at 3375 cm<sup>-1</sup>, 2925 cm<sup>-1</sup>, 2390 cm<sup>-1</sup>, 1628 cm<sup>-1</sup>, 1338 cm<sup>-1</sup>, 1125 cm<sup>-1</sup> and 627 cm<sup>-1</sup>. The presence of band at 1628 cm<sup>-1</sup> is due to presence of TiO<sub>2</sub> [9] while band at 1338 cm<sup>-1</sup> indicates S=O induced from titanium sulphate [10] and band at 1125 cm<sup>-1</sup> represents sulphates [11], which is not the case in pure TiO<sub>2</sub> as shown in Figure 3. This proves that there is chemical adsorption or penetration of SO<sub>4</sub><sup>2-</sup> ions into the crystal lattice of TiO<sub>2</sub>.

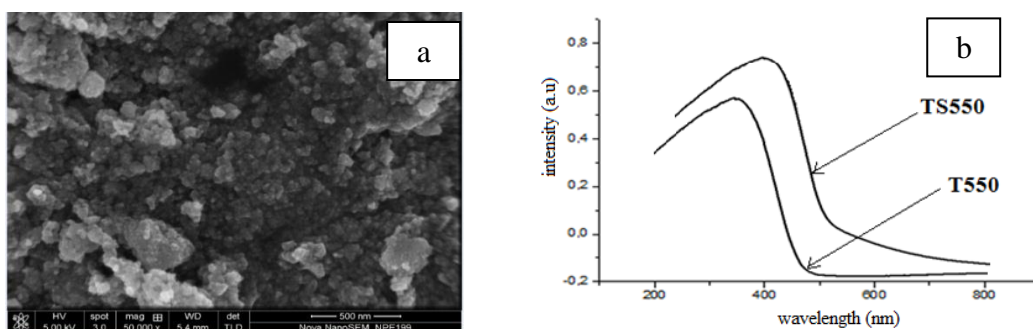


Figure 4. SEM image of TS550 (a) and UV-vis absorption spectra of T550 and TS550 (b).

SEM image (Figure 4a) shows the typical shape of TS550 particles are quite uniform and the average size of particles are about 20 nm.

UV-vis absorption spectra in Figure 4b shows that after being modified by sulfur,  $\text{TiO}_2$  can absorb radiation in visible region. Spectrum of T550 shows a relatively weak absorption from about 400 nm. It totally agrees with the fact that band gap energy of titania in anatase form is 3.2 eV, which is equivalent to photon with wavelength about 382 nm. Modification of titania with sulfur has significantly changed light absorption ability of catalyst. It can be seen that absorption of TS550 at larger wavelength and has absorption maximum at 404 nm with band gap 3.07 eV. Absorption spectrum successfully proves that modification of titania with sulfur can shift working region of catalyst into visible region.

Chemical composition of T550 and TS550 materials were characterized by EDS spectra (Fig. 5).

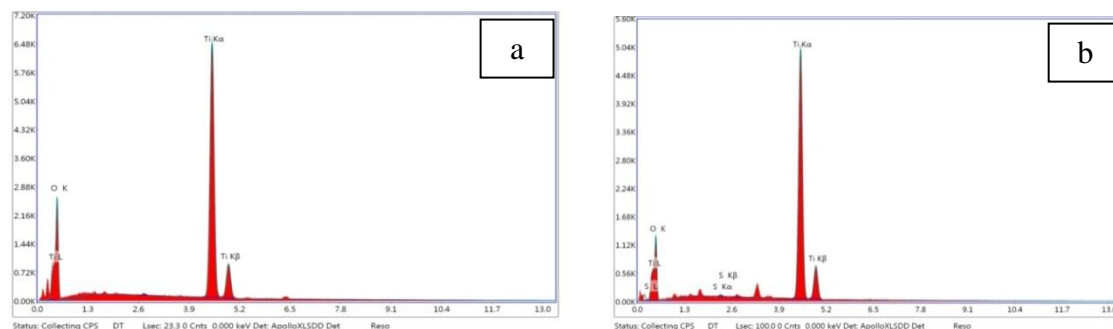


Fig. 5. EDS spectra of T550 (a) and TS550 (b).

EDS spectra in Figure 5a shows that T550 sample only contained peaks of Ti and O elements, which can be attributed to composition of  $\text{TiO}_2$ . The EDS spectra of TS550 material was shown in Figure 5b. It can be seen that  $\text{TiO}_2$  modified by sulfur contained peaks of Ti, O and S elements, there are no peaks of other elements on the EDS spectra. This proves that the present of sulfur in TS550 sample.

To determine surface area of TS550 material and pore size, the catalyst was characterized by BET. Results were shown in Figure 6.

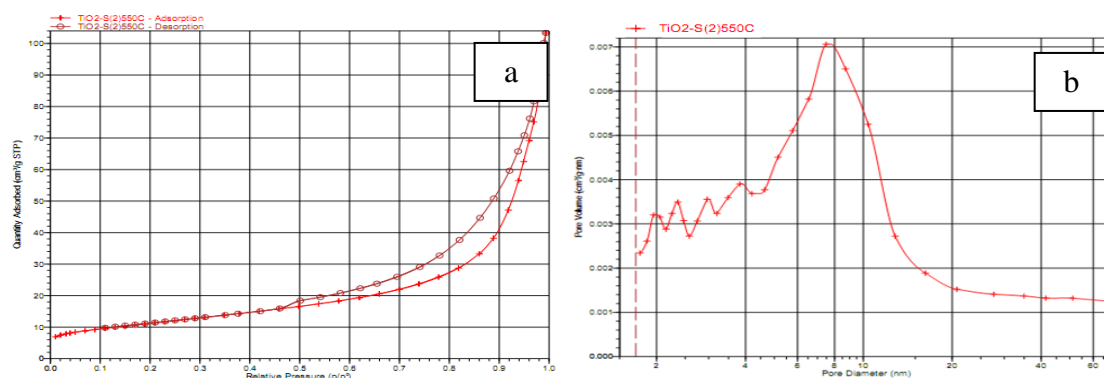


Figure 6. Adsorption – desorption isotherms diagram (a) and pore size distribution (b) of TS550.

From Figure 6a, TS550 has surface area of 40.44 m<sup>2</sup>/g. The sharp decline in desorption curve and the hysteresis loop at high relative pressure means that TS550 belong to mesoporous type, both materials has type IV curve as classified by IUPAC. From Figure 6a pore size distribution is calculated from the corresponding desorption branch of each isotherm by Dollimore – Heal method. TS550 has narrow peaks and most pores have size of about 8 nm.

### 3.2. Tests on photocatalytic activity of T550 and TS550

Experiments testing effect of amount of sulfur to methylene blue degradation were carried out at the same conditions (600 mL 10 ppm methylene blue solution, 0.20 g TS550 catalysts and 3 hours for the reaction) under compact lamp light.

Table 1. Conversion of methylene blue using S-TiO<sub>2</sub> with different amounts of sulfur.

S/TiO <sub>2</sub> mole ratios (%)	Conversion (%)	S/TiO <sub>2</sub> mole ratios (%)	Conversion (%)
10	34.87	25	67.06
15	57.30	30	55.67
20	63.02	40	41.73

Photocatalytic efficiency is not a function of the amount of sulfur (Table 1). It increases with the amount of sulfur up to a certain value (25 % S/TiO<sub>2</sub> mole ratio). Exceeding this threshold value leads to decrease of efficiency. This dependence of photocatalytic activity on the amount of sulfur can be suggested that up to a certain amount, sulfur can become recombination centers, where electrons and holes meet.

The experiments of methylene blue degradation were carried out simultaneously on T550 or TS550, one with solar light (from 8 am – 11 am per day) and compact lamp light and one in the dark. All other conditions (600 mL 10 ppm methylene blue solution, 0.20 g T550 or TS550 catalysts and 3 hours for the reaction) are kept the same. Results were shown in Table 2.

Table 2. Methylene blue degradation using T550 and TS550 under different light sources.

Catalysts	Conversion (%)		
	Compact lamp	Solar	Dark
<b>T550</b>	23.58	35.86	14.46
<b>TS550</b>	67.06	79.16	15.12

Results in Table 2 indicate that the methylene blue conversion decreased insignificantly for experiments in the dark (14.46 % for T550 and 15.12 % for TS550). However, when light is on, efficiency of TS550 in methylene blue degradation is higher than T550, which means that TiO<sub>2</sub> modified by sulfur can improve catalytic activity of TiO<sub>2</sub> under solar radiation.

Data in Table 2 show that after 180 min, methylene blue removal efficiency on TS550 reaches 79.16 % when using solar as light source, while it is only 67.06 % if experiments were carried out with compact lamp light. This observation is understandable because photon in solar light (about 7 % UV radiation) is stronger compact lamp light.

#### 4. CONCLUSION

Modification of TiO<sub>2</sub> by sulfur enhanced the photocatalytic activity of the TiO<sub>2</sub> leading to effective use of the synthesized materials even under visible light region. The obtained results indicated that sulphate ions adsorbed or penetrated of into the crystal lattice of TiO<sub>2</sub> leading to decrease band gap energy of titania in anatase form from 3.2 eV to 3.07 eV. The optimal S/TiO<sub>2</sub> mole ratio leading to maximum increase in photocatalytic activity of the S doped TiO<sub>2</sub> was 25%. The synthesized materials working well even under visible light region opened a new trend on application of the photocatalyst for treatment of various organic pollutants in wastewater.

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