MINISTRY OF EDUCATION AND TRAINING
QUY NHON UNIVERSITY

NGUYEN THI LAN

PREPARATION OF (C, N, S)-TIO_2 MATERIALS FROM BINH DINH ILMENITE ORE FOR THE TREATMENT OF WASTEWATER FROM SHRIMP FARMS

Speciality : **Physical and Theoretical Chemistry**

Code : **9 44 01 19**

PhD THESIS OF CHEMISTRY

Binh Đinh, 2020

The study is carried out at:

University of Education, Quy Nhon University

Supervisors: Asc. Prof. NGUYEN PHI HUNG
Dr. LE THI THANH THUY

Reviewer 1: Prof. TRAN THAI HOA

Reviewer 2: Prof. DUONG TUAN QUANG

Reviewer 3: Asc. Prof. LE TU HAI

The thesis was assessed by University Examination Board at Quy Nhon University, An Duong Vuong Str. 170, Quy Nhon city, Binh Dinh Province.

At ….., ………, 2020.

The thesis can be found at:

- Library of Quy Nhon University
- Vietnam National Library (31 Trang Thi Str., Hoan kiem, Ha noi)

I. INTRODUCTION OF THESIS

1.The imperativeness of thesis

Brackish shrimp farming appeared in our country very early and increasingly plays an important role in aquaculture. Up to now, shrimp farming has developed strongly with increasing intensification level, along with that, export value has grown strongly, accounting for more than 40% of total seafood industry turnover. However, at present, agriculture in general and fishery in particular have to deal with the situation of people arbitrarily using antibiotics in animal husbandry and aquaculture, not following the instructions of the authorities, leading to high antibiotic residues in livestock products as well as the environment, adversely affecting consumer health, causing great difficulties in managing and affecting export activities. In particular, the current wastewater from shrimp ponds is almost untreated before being discharged into the environment and has been causing increasingly serious environmental pollution. Therefore, the problem of wastewater treatment before shrimp discharged into the environment should be properly studied.

TiO_2 with superior properties such as photocatalytic activity is high, durable, non-toxic, ... is being studied and applied widely. However, with a band gap of about 3.2 eV, TiO_2 material can only give a catalytic effect in ultraviolet (UV) light. The portion of ultraviolet radiation in the solar spectrum to the earth's surface is only about 5%, so the use of this source of radiation for environmental treatment with TiO_2 photocatalyst is limited. In order to expand the use of solar radiation energy both in the visible light area into the photocatalytic reaction, it is necessary to reduce the forbidden energy of TiO_2 or shift the absorption of TiO_2 light from the ultraviolet region. to the visible region.

In Vietnam TiO_2 used as a photocatalyst is often prepared from the original precursors such as alkoxide, sulfate salt, chloride salt of titanium so it has a high price. Meanwhile, the source of titanium-containing materials in Vietnam in general is plentiful and Binh Dinh is one of four provinces assessed to have titanium ore with great potential of the whole country, with reserves of about 2.5 million tons, but ineffective exploitation and use

From the above problems, we was carried the thesis with the title of ***"Preparation of (C, N, S)-TiO_2 materials from Binh Dinh Ilmenite ore for the treatment of wastewater from shrimp farms"***

2. The task of the thesis

- Preparation of TiO_2-based materials from Binh Dinh Ilmenite ore by sulfate method and surface modify by non-metals C, N, S;
- Treatment of a number of pollutants in shrimp waste water using modified TiO_2 material prepared from Ilmenite Binh Dinh ore in combination with biological treatment method.

3. Scope and object of the thesis

In the thesis, scope and object of the study are selected:

- TiO_2 nanomaterial modified by non-metal prepared from Ilmenite ore in Binh Dinh; Shrimp wastewater is taken from Tuy Phuoc district, Binh Dinh province.
- Research and preparation of TiO_2 material from Ilmenite Binh Dinh ore by sulfate method; synthesizing TiO_2 modified C, N, S materials by hydrothermal method; Investigate photocatalytic activity of materials by tetracycline antibiotic decomposition reaction in aqueous solution; Investigate the possibility of treating wastewater from shrimp farming in reality by photocatalytic method based on modified TiO_2 material combined with biological treatment method.

4. Scientific and practical meaning of the thesis

Scientific significance: Preparing C-N-S tridoped TiO_2 materials from Ilmenite ore, developing a photocatalyst reaction to decompose tetracycline antibiotics and determining the best conditions of modified TiO_2 materials .

Practical significance: Contributing to deep processing of Ilmenite minerals, increasing the value of exploiting natural resources. The preparation TiO_2 material is applied to shrimp wastewater treatment by photocatalytic method combined with biological method.

The results of the thesis show that the research is likely to be extended to apply in the treatment of polluted water and water color solution in water; catalyze the oxidation reaction of some organic compounds.

5. Originality of the thesis

- For the first time, studying doping elements C, N, S into TiO_2 nano materials prepared from Ilmenite source in Binh Dinh, exploiting the function of C-N-S tridoped TiO_2 materials in improving photocatalytic activity of TiO_2 nanomaterials.
- Develop photocatalytic reaction mechanism, identify intermediate products of C-N-S tridoped TiO_2 materials in tetracycline antibiotic decomposition by HPLC-MS method.
- Application of C-N-S tridoped TiO_2 materials into the wastewater treatment of shrimp culture by photocatalytic methods combined with biological methods.

6. The lay-out of the thesis

The thesis possesses 135 pages, includes: Introduction (3 pages); Chapter 1: Theory overview (36 pages); Chapter 2: Content and methods (23 pages); Chapter 3: Results and discussion (44 pages); Conclusion and request (2 pages); List of publishing manuscripts (1 page); Reference (26 pages).

II. CONTENT OF THE THESIS

Chapter 1. Theory overview

Searching and collect scientific information related to TiO_2 nano materials on synthetic methods and applications. From that choose the suitable methods and application for the thesis. Finding originality that did not mention in reference to carry out the thesis.

The overview shows that modified TiO_2 nanomaterials have been studied a lot. Special TiO_2 denatured by metals, non-metals or composite composites. In which, the applications C-N-S tridoped

TiO_2 materials prepared Ilmenite ore and thiourea iron in the field adsorption, photocatalytic and catalyzing oxidation reactions of organic compounds is limited. Therefore, the thesis also aims to study the applications of this material in the fields of adsorption and catalysis.

CHAPTER 2. OBJECTIVES AND METHODS

2.1. Objectives

- Preparation of TiO_2 material from Ilmenite Binh Dinh ore by sulfate method;
- Study preparing C-N-S tridoped TiO_2 materials and Investigation of influencing factors through the breakdown of tetracycline antibiotics.
- Application of modified TiO_2 material to handle a number of pH, COD, BOD_5, NH_4^+, TSS and antibiotics in shrimp wastewater from biological methods combined with photocatalytic methods.

2.2. Methods

The thesis has used structural characteristics methods includes: includes: X-ray diffraction (XRD) studying crystal phase composition, Fourier-transform infrared spectroscopy (FT-IR) realizing oxygen containing groups on the surface of material, X-ray photoelectron spectroscopy (XPS) is spectroscopic technique that measures chemical state and electronic state of the elements that exist within a material, energy-dispersive X-ray spectroscopy (EDS) analyzing atomic compostion, nitrogen adsorption/desorption isotherms analyses determining surface area, canning electron microscope (SEM) and transmission electron microscope (TEM) observing morphology and size of particle, Visible diffuse ultraviolet reflectance (UV-Vis - DRS) method to determine the band gap energy of a material; Photoluminescence method (PL) determines the recombination ability of electrons and photoluminescent holes.

Using analytical methods including: Liquid chromatography combined with mass spectrometry (HPLC-MS) to identify intermediate compounds after antibiotic decomposition.

2.3. Experimental

- Prepare TiO_2 material;
- Synthetic C-N-S tridoped material;
- C-N-S tridoped material for used for photocatalytic for tetracycline antibiotic degradation.
- Wastewater treatment of shrimp farming by biological method combined with photocatalytic method.

CHAPTER 3. RESULTS AND DISCUSSION

3.1. Preparation of TiO_2 material from Ilmenite Binh Dinh

3.1.1. Characterization of TiO_2

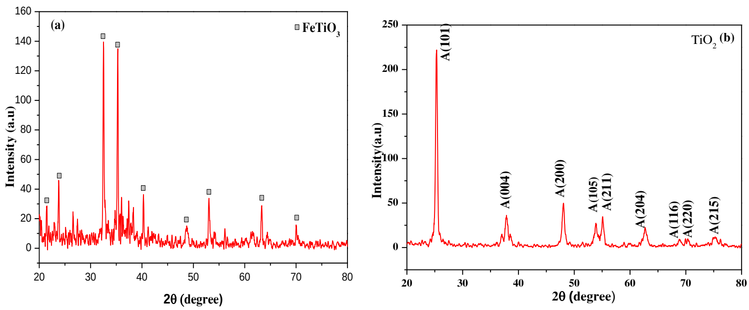

Fig 3.1. XRD patterns of:(a) Ilmenite ore;(b)TiO_2 material

The obtained materials were studied by XRD measurements (Fig 3.1). It was found that that the main component of Ilmenite (a) ore is FeTiO3 (PDF NO. 29-0733) and the crystal structure of TiO_2 (b) in anatase phase with diffraction peaks featured at the corner 2θ = 25,25; 37,88; 48,45; 53,9; 55,0 và 62,6^o (standard card JCPDS 21-1272). The crystallite sizes of the samples could be estimated from the broadening of the X-ray diffraction peak according to Scherrer formula. It was calculated that TiO_2 has an average crystallite size of 14.39 nm.

The IR spectra shown in Figure 3.2 show characteristic diffraction peaks at the wave numbers 3428.9; 1632.5; 467 cm^{-1}. In particular, the diffraction peaks at 3428.9 and 1632.5 cm^{-1} were referred to the variation and deformation oscillations of the O-H bonds in the adsorbed water molecules on the surface. The maximum peak between 400 - 500 cm^{-1} is thought to be the valence oscillation of Ti-O bond of TiO_2.

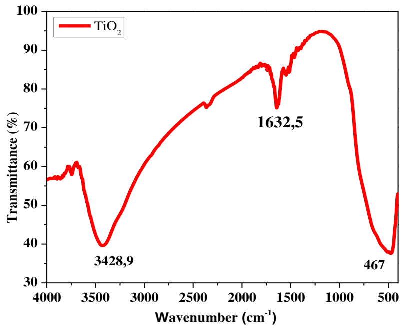

Fig 3.2. FT-IR spectra TiO_2

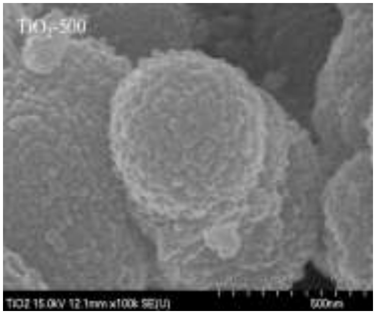

Fig 3.3. SEM images of TiO_2

SEM image (Fig 3.3) results show that the collected TiO_2 particles are spherical, the particles are relatively uniform.

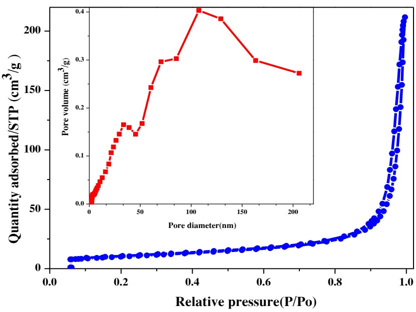

Fig 3.4. Nitrogen adsorption/desorption isotherms of TiO_2

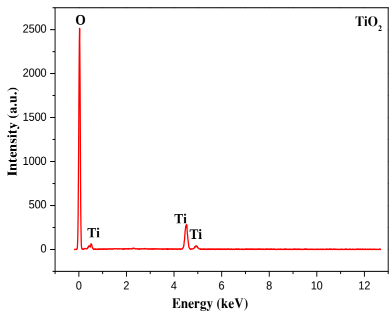

Fig 3.5. EDX spectra of TiO_2

The results in Figure 3.4 show that the adsorption and desorption isotherm curves of the sample sample TiO_2 of type IV with hysteresis type H1 are all typical for the average capillary structure. On the isothermal adsorption-desorption line N_2 of TiO_2

sloping sharply at the relative pressure area P/Po = 0.9 - 1.0, characteristic for large capillaries and small delay due to capillary condensation governing. This suggests that TiO_2 particles may have bonded together to create large capillaries, with an average capillary diameter according to BJH of 36.69 nm. The capillary size distribution line extends over 50 nm for a large but uneven capillary.

The EDX spectrometer in Figure 3.5 indicates that the TiO_2 material prepared consists of the main elements titanium, oxygen, respectively% by mass of 22.61 and 76.74%. The purity reaches 99.35%, the impurity constitutes 0.65%, this shows that the obtained TiO_2 material has a high purity, the basic ingredient is TiO_2.

The optical properties and forbidden energy values of TiO_2 were determined by UV-Vis-DRS method, the results are shown in Figure 3.6. By extrapolating the curve in Figure 3.6, the band gap of TiO_2 anatase phase is 3.2 eV. Absorption of light from the wavelength of 187 nm and ends at the wavelength of 387 nm in the ultraviolet region.

3.1.2. Photocatalytic activity of Ilmenite mineral and TiO_2 material

Figure 3.7 presents the kinetics of TC degradation over TiO_2 and raw ilmenite. As can be seen in the figure, ilmenite does not exhibit any photocatalytic activity toward to oxidize TC due to the chemical inert property of ilmenite mineral. For TiO_2, the dark adsorption/desorption equilibrium is reached after 30 min and it displays adsorption capacity TiO_2 about 14,69% and TiO_2 yields a degradation efficiency about 50% after 120 min of visible light illumination.

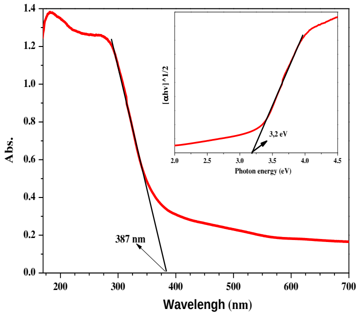

Fig 3.6. UV-Vis – DRS spectra of TiO_2

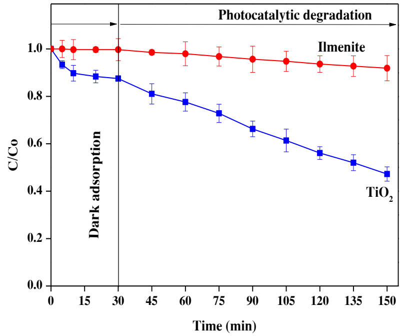

Fig 3.7. Kinetics of TC decomposition reaction

3.2. MODIFIED TiO_2 MATERIAL

3.2.1. Effect of molar ratio between thiourea/TiO_2 in C, N, S co-doped TiO_2 material with photocatalytic activity

3.2.1.1. Characteristic of C, N, S co-doped TiO_2 material

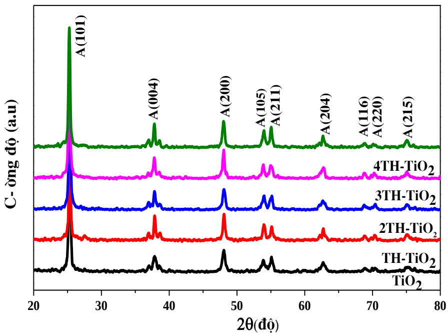

Fig 3.8. XRD patterns of TiO_2 amd xTH-TiO_2 (x = 1, 2, 3, 4)

From the XRD diagram in Figure 3.8, it is shown that the diffraction peaks of the xTH-TiO_2 doped samples are similar to those of TiO_2 material, but the intensity varies. The results show that TiO_2 and xTH-TiO2 materials contain spectral peaks of $2\theta = 25.3^o$; 37.8^o; 48.1^o; $53,9^o$; $55,0^o$; $62,6^o$; 68.8^o; 70.3^o; 75.1^o corresponds to the lattice facets (101), (004), (200), (105), (211), (204), (116), (220),

(215) of the anatase phase. From the above results, it can be concluded that thiourea doping does not affect the formation of TiO_2 phase structure.

IR spectra of thiourea, TiO_2 and xTH-TiO_2 samples in the range of 400 - 4000 cm^{-1} are shown in Figure 3.9. Absorbent peaks of about 3400 cm^{-1} and peaks at 1638 cm^{-1} are signals, respectively, characterizing valence and deformation fluctuations of the OH bonding of adsorbed water molecules on the surface and of hydroxyl groups. on the material surface.

The peak at 2330 cm^{-1} wave number characterizes the covalent oscillation of the C = O bond of the CO_2 molecule adsorbed on the surface of the material. Absorption range in the range 1516-1567 cm^{-1} corresponds to the nitrate ligand. According to A. Brindha et al., The wave number at 1441cm^{-1} characterizes the Ti-O-N bonding group. In the region below 1000 cm^{-1}, a number of peaks are assigned to the absorbance bands of the strain oscillation of the Ti-O-Ti, Ti-O and O-Ti-O bonds.

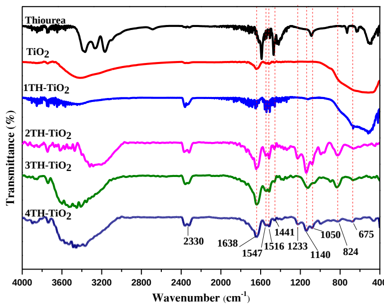

Fig 3.9. FT-IR spectra of thourea, TiO_2 and xTH-TiO_2 (x = 1, 2, 3, 4,)

According to Cheng et al., The peaks at wave numbers 1233, 1140 and 1050 cm^{-1} can be attributed to the characteristic oscillation from the bilge ligand of the S-O groups to the Ti^{4+} ions. Obviously, compared with pure TiO_2, the simultaneous doping of three elements C, N, S into TiO_2 increased the adsorption of water molecules and hydroxyl groups on the surface to create electron traps to improve efficiency. Electrolysis results and photoelectric holes enhance the photocatalytic decomposition of TC solution.

The band gap energy of xTH-TiO_2 samples determined by Kubelka – Munk (Fig 3.11) is lower than that of TiO_2 material, in which 2TH-TiO_2 material have the lowest band energy of 2.88 eV.

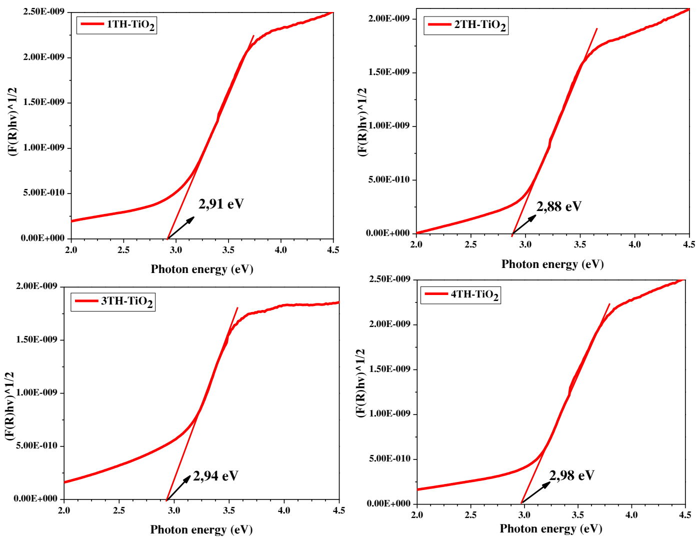

Fig 3.11. Graph of dependence of Kubelka-Munk function on photon energy to estimate Eg of material samples xTH-TiO_2

3.2.1.2. Photocatalytic activity of materials

The ability to decompose TC of materials xTH-TiO_2 is shown in Fig 3.12 and Fig 3.13. The results showed that when the molar ratio increased, the catalytic activity increased but not uniformly. The 2TH-TiO_2 ratio is considered to be an appropriate doping ratio to produce materials with high photocatalytic activity.

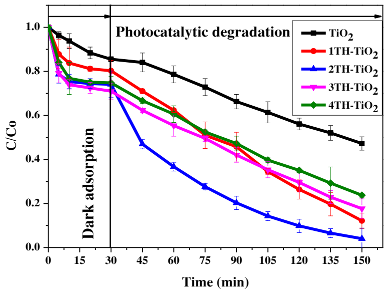

Fig 3.12. The change in C/Co as a function of time for TiO_2 và x$TH-TiO_2$

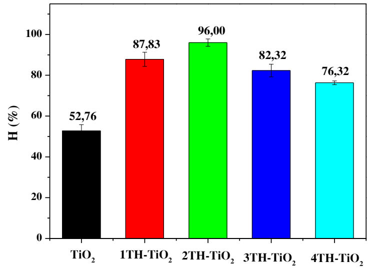

Fig 3.13. Effect of function amount of doping to decomposition efficiency TC

3.2.2. The effect of hydrothermal temperature of modified TiO_2 material on photocatalytic activity

3.2.2.1. Characteristic of C, N, S co-doped TiO_2 material at hydrothermal temperatures

Fig 3.14 show that, the 2TH-TiO_2-T material samples at different hydrothermal temperatures all have characteristic diffraction peaks of $2\theta = 25.3^o$; 37.8^o; 48.1^o; $53,9^o$; $55,0^o$; $62,6^o$; 68.8^o; 70.3^o; 75.1^o corresponds to the lattice surfaces (101), (004), (200), (105), (211), (204), (116), (220), (215) of the anatase phase. As the hydrothermal temperature increases, the intensity of the diffraction peaks increases, the width of the diffraction pins becomes narrower, the crystal size increases, the material has a high degree of crystallinity.

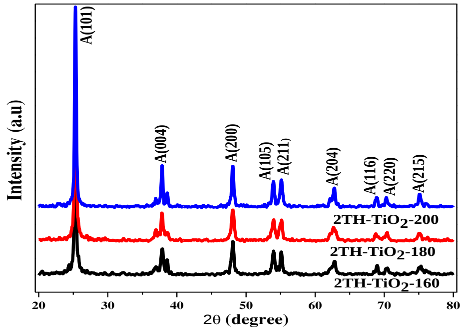

Fig 3.14. XRD patterns of 2TH-TiO_2-T (T=160 ^oC,180 ^oC và 200 ^oC)

3.2.2.2. Photocatalytic activity of 2TH-TiO_2-T material samples by hydrothermal temperature

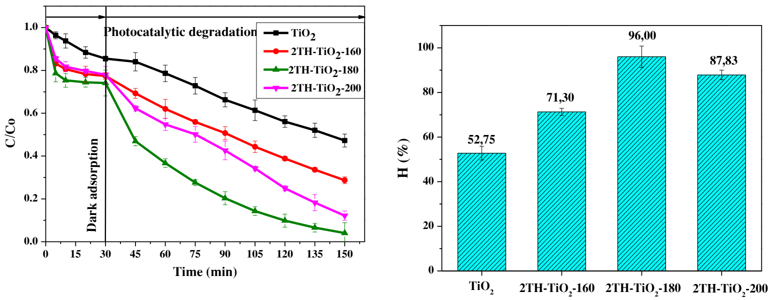

Fig 3.15. (a) Kinetics of TC decomposition reaction; (b) The effect of hydrothermal temperature on TC decomposition efficiency

Hydrothermal temperature has a great influence on the photocatalytic activity of materials. Initially, when the hydrothermal temperature was increased, the photocatalytic activity of the material increased, increasing from 71.30% to 96.00%. However, if the temperature continues to rise, the catalytic activity of the material decreases, the catalytic activity of the 2TH-TiO_2 material reaches only 87.83%. Photocatalytic activity of the doped samples is higher than that of TiO_2.

3.2.3. Influence temperature of modified TiO_2 material on photocatalytic activity

3.2.3.1. Characteristic of C, N, S co-doped TiO_2 materials at different firing temperatures

It is found that all TH-TiO_{2-a} samples crystallized in the anatase phase, no rutile or brookite phases are observed. As the annealing temperature increases from 400 to 700 ^oC, the (101) peak intensity increases and the spectral line half width at the (101) plane became narrower, resulting in a larger crystallite size. This proves that TiO_2 anatase gradually crystallizes as the annealing temperature increases. The average crystallite size of the 2TH-TiO_2-400, 2TH-TiO_2-500, 2TH-TiO_2-600, 2TH-TiO_2-700 samples are 9.07; 9.54; 9.79; 13.4 nm.

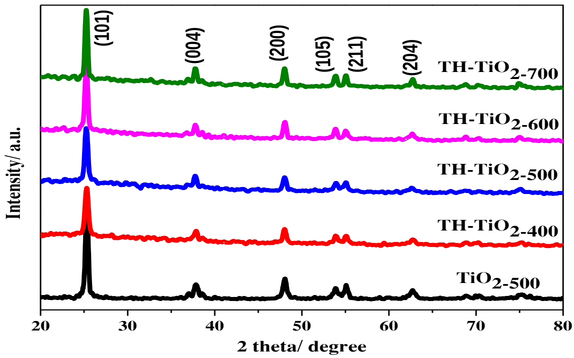

Fig 3.16. XRD patterns for TH-TiO_{2-a} annealed at different temperatures

The specific surface area and porosity of the obtained samples were determined by the BET method and their results are presented in Fig 3.17.

The specific surface area determined according to the BET method for the TH-TiO_{2-a} samples annealed at 400 - 700 ^oC is 73.47, 92.25, 65.20 and 47.35 m^2/g, respectively.

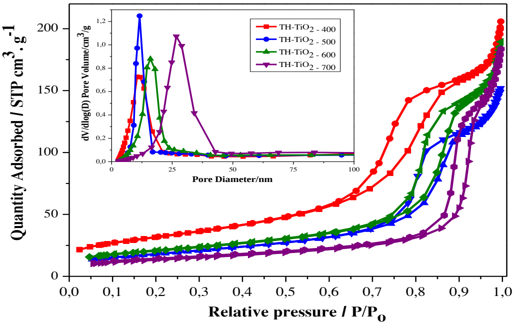

Fig 3.17. N_2 adsorption-desorption isotherms at 77 K and pore diameter distribution curves of the TH-TiO_{2-a} samples according to BJH

The surface morphology of the TH-TiO_{2-a} samples are characterized by TEM and SEM methods and the results are shown in Fig 3.18 and Fig 3.19 .

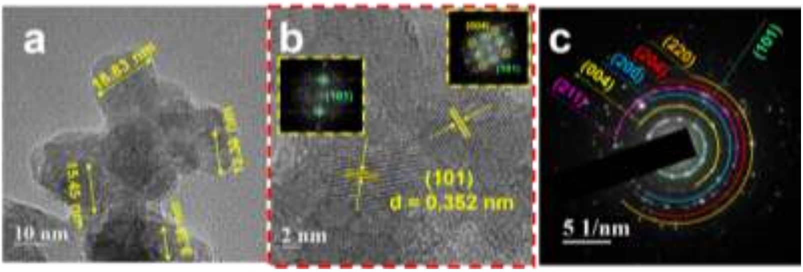

Fig 3.18. (a,b) HR-TEM images with consistent Fast Fourier Transform (FFT) in insets, and (c) Selected Area Electron Diffraction (SAED) of TH-TiO_2-500.

The construction of secondary particles from sub-one could be clarified in HR-TEM images (as shown in Fig. 3.18a) which indicates that the size range of the primary particles is around 12 to 18 nm. The high magnification TEM image in Fig 3.18b displays the observable lattice fringe corresponding to (101) plane with distance of 0.352 nm which is confirmed by Fast Fourier Transforms (FFT) (insets). The acceptable crystallinity of obtained sample was further proved via Selected Area Electron Diffraction (SAED) (Fig. 3.18c) which includes separated rings formed form clear spot. The corresponding lattice planes were also indexed in SAED pattern.

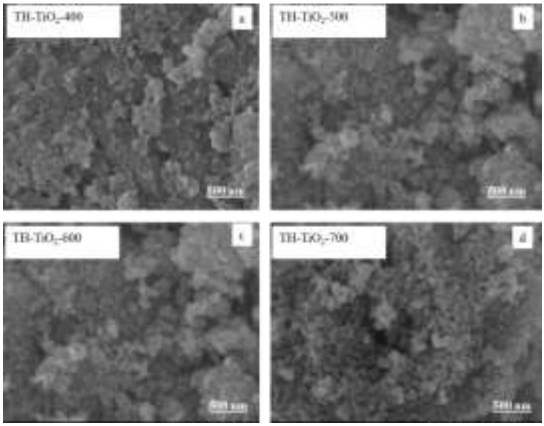

Fig 3.19. SEM images of TH-TiO_{2-400} (a), TH-TiO_{2-500} (b), TH-TiO_{2-600} (c), TH-TiO_{2-700} (d)

As can bee seen in Fig 3.19, the obtained samples have a structured morphology, the particles are spherical, quite uniform.

The band gap energy of all samples was calculated based on the Kubelka-Munk equation and shown in Fig 3.21.

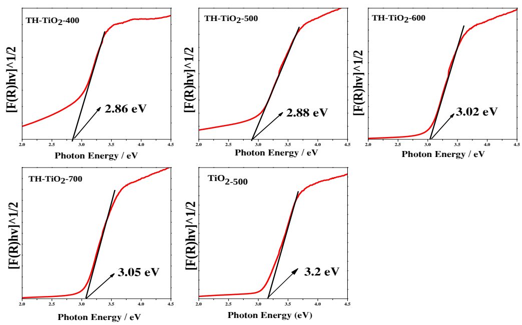

Fig 3.21. Kubelka-Munk function versus photon energy for band gap estimation

The oxidation states of C, N and S in TH-TiO_2 were studied by XPS spectra (Fig 3.22). The survey XPS spectrum (Figure 3.22) presents Ti2p peaked at 459.36 eV; C1s at 284.70 eV; O1s at 531.00

eV; N1s at 400.30 eV; and S2p at 168.01 eV. This shows that there has been doping of elements C, N, S into TiO_2 lattice.

The photoluminescence (PL) is widely used to study the recombination of photo-induced electron/hole pairs. The PL spectra of TiO_2 and TH-TiO_2 materials are shown in Fig 3.23. The materials were excited at 404 nm with a strong emission peak at about 468 nm. It was found that there is a significant decrease in luminescence intensity of TH- TiO_2 compared to TiO_2.

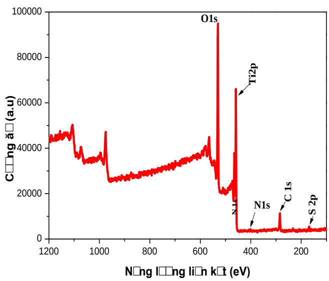

Fig 3.22. XPS spectrum of 2TH-TiO_2-500

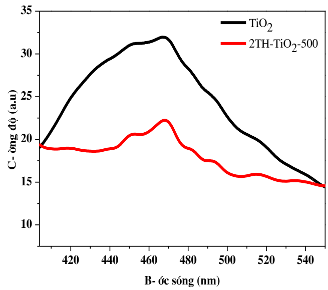

Fig 3.23. PL spectra of TiO_2 and TH-TiO_2

3.2.3.2. Photocatalytic activities

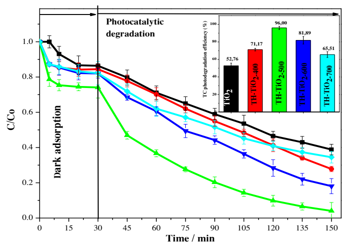

Fig 3.24. The change in C/Co as a function of time for TiO_2-500 và TH-TiO_2-a (a = 400, 500, 600 and 700 ^oC), tetracycline concentration of 30 mg/L

The tetracycline photocatalytic degradation of TH-TiO_2-a and TiO_2-500 samples is shown in Fig 3.24. It is worth mentioning that all C, N and S co-doped TiO_2 samples yield a higher photodegradation efficience than the undoped TiO_2 sample. Particularly, the TH-$TiO_{2\text{-}500}$ show the best photocatalytic activity under the visible light irradiation (96 %).

3.2.4. Experimental factors affecting the interactive optical activity of C, N, S co-doped TiO_2 materials

3.2.4.1. Effect of initial TC concentrations

In this experiment, the initial TC concentration varied from 30 to 70 mg.L^{-1}, the other experimental conditions remained the same. It was found that when increasing the initial TC concentration from 30 to 70 mg.L^{-1} decomposition efficiency decreases significantly from 96% to 55% after 120 minutes of visible-light illumination (Fig 3.25a). At the initial concentrations of 40 mg/L, 50 mg/L and 60 mg/L, TC degradation efficiency is also significantly reduced. Thus, the appropriate initial concentration for TC decomposition of 2TH-TiO_2 samples is 30 mg/L.

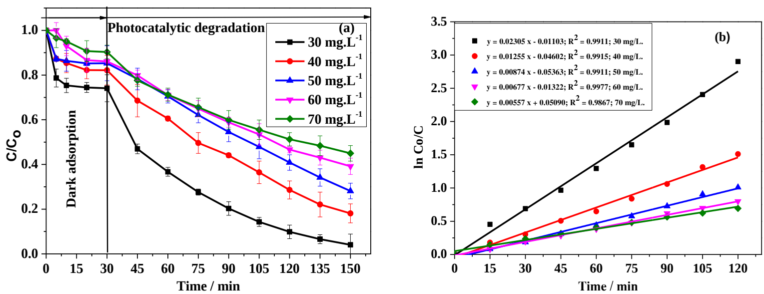

Fig 3.25. a) Kinetics of TC decomposition reaction; b) Plot of Langmuir-Hinshelwood model at different TC initial concentrations. (Conditions: C_0 = 30 mg.L^{-1}, V =100 mL, m_{Cat} =0.06 g)

The Langmuir-Hinshelwood model was employed to analyze the kinetics data in which the linear plot of $\ln(C_t/C_o)$ *vs.* t is constructed. Fig 3.25b presents the Langmuir-Hinshelwood plots at different concentrations. The high determination coefficients, R^2

(0.99 – 1) confirm that the kinetic degradation reaction of TC over TH-TiO_2 fixed well the Langmuir-Hinshelwood model.

3.2.4.2. Effect of pH

The pH of point of zero charge (pH_{PZC}) of TH-TiO_2 calculated by the pH drift method is 4.5 (Fig 3.26a). Thus, at the pH of solution <2.5 (pH <pKa = 3.3) of TC is related to acid ionization. OH group is at position 3, dimethyl amino group is protonized in acid environment, TC ions are positively charged, so there is an electrostatic repulsion between TC cation and negative surface of the material. to reduced TC adsorption efficiency. When pH> 8 (pH> pKa = 7.5) amino protons are lost, the negatively charged TC ions increase the repulsion between the anion TC and the positively charged material surface. At the natural pH range of 4.5, the TC solution exists in the form of bipolar ions, the surface of the material is not charged, electrostatic repulsion does not occur making the highest TC decomposition efficiency.

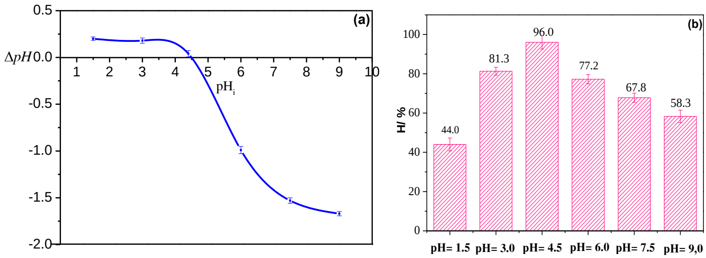

Figure 3.26. a) Effect of pH on the TC degradation efficiency; b) The pH_{PZC} determined by pH drift method.

3.2.4.3. Reusability

Reusability is one of the very important factors when deciding to choose a catalyst for economic and environmental purposes.

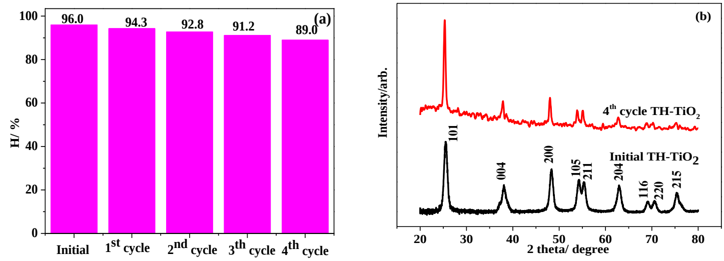

Figure 3.28. a) TC degradation efficiency after four reuse cycles of TH-TiO_2; b) XRD patterns of reused TH-TiO_2.

The used TH-TiO_2 material was washed many times with distilled water and dried at 80°C for 12 hours for regeneration. The TC degradation efficiency over reused catalyst is presented in Fig 3.28a. This result shows a slight reduction in TC decomposition efficiency, but after four reuse times, effective TC decomposition still reached over 89.0 %. The XRD patterns of TH-TiO_2 (Fig 3.28b) seems slightly changeable indicating TH-TiO_2 possessed excellent structural stability that after the regeneration process.

3.2.5. Mechanism of photocatalytic reaction

The effect of extinguishing agents on TC degradation performance is shown in Fig 3.29 and 3.30. In general, the presence of free radicals reduces the efficiency of TC degradation. AO (quenching h^+), BQ (quenching $^{\bullet}O_2^-$), and BN (quenching e^-) reduce significantly degradation rate of TC. However, TB seems not to affect TC degradation. This concludes that the free radicals (h^+; $^{\bullet}O_2^-$; e^-) take mainly part in degradation reactions of TC while $^{\bullet}OH$ is negligible.

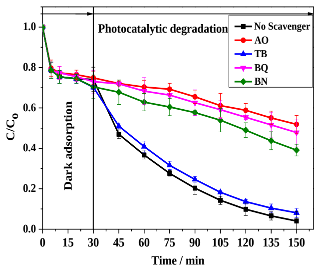

Fig 3.29. Kinetics of TC degradation on TH-TiO_2 in the presence of different scavengers.

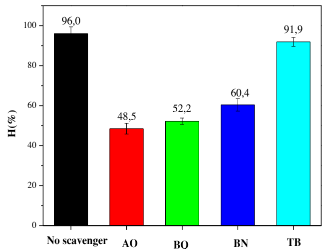

Fig 3.30. Effect of quencher on TC decomposition performance

These free radicals are strong oxidizing agent which could oxidize partially or complexly TC. The arguments are illustrated in the Fig 3.31 and equations (1) to (6).

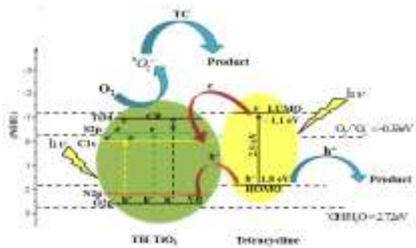

Fig 3.31. The mechanisms of charge carrier migration and free radicals formation on TH-TiO_2 catalyst under visible light illumination

$$TC + h\nu \rightarrow TC(e^-_{CB} + h^+_{VB})$$

$$2TH - TiO_2 + h\nu \rightarrow 2TH - TiO_2(e^-_{CB} + h^+_{VB})$$

$$TC(e^-_{CB} + h^+_{VB}) + 2TH - TiO_2 \rightarrow 2TH - TiO_2(e^-_{CB}) + TC(h^+_{VB})$$

$$2TH - TiO_2(e^-_{CB}) + O_2 \rightarrow {}^{\bullet}O_2^- + 2TH - TiO_2$$

$$2TH-TiO_2(h^+_{VB}) + TC \rightarrow TC(h^+_{VB}) \rightarrow \text{Phân hủy}$$

$$H_2O \rightarrow H^+ + OH^-$$

$$H_2O + 2TH-TiO_2(h^+_{VB}) \rightarrow H^+ + {}^{\bullet}OH$$

$$^{\bullet}O_2^-, h^+, {}^{\bullet}OH + TC/TC^* \rightarrow \text{Degradation products}$$

3.3. RESULTS ON SHRIMP TREATMENT OF SHRIMP MATERIAL OF TiO_2 MATERIALS VARIED BY BIO-METHODS COMBINED WITH CATHOLIC OPTICAL METHOD

3.3.1. Assessing the quality of initial wastewater

Waste water from shrimp ponds comes from Phuoc Thuan commune, Tuy Phuoc district. The analysis of the input water quality shows that most of the indicators (except pH) exceed the permitted level of waste water discharged into the environment, especially the tetracycline antibiotic indicator exceeds the permitted level by more than 12 times. . Therefore, it can be concluded that wastewater from shrimp ponds is a serious source of pollution. Therefore, it is necessary to treat wastewater sources to ensure these quality standards before discharging into the environment.

3.3.2. Investigate the possibility of treating wastewater from shrimp farming by biological methods

3.3.2.1. Investigation of optimal conditions for the treatment of criteria in shrimp wastewater, with Remediate probiotics

Remediate is a probiotic consisting of a series of microorganisms that treat water environment, selected from Bacillus strains, which convert organic and ammonium. Experiments on aerobic environment with different VSV concentrations 3 ppm, 4 ppm, 5 ppm, 6 ppm and 7 ppm in order to find the optimal conditions for the activity of these bacterial strains in the treatment of waste water environment for shrimp ponds. The optimal concentration is defined as 7 ppm.

3.3.2.2. Results of wastewater treatment by shrimp biological methods

The result of microbiological processing ability is shown in Fig 3.39. Experimental results show that the effectiveness of using probiotics to treat wastewater, most of the targets have reached the discharge standards, but the COD value is much higher than the discharge standard, This shows that this waste water source contains many persistent organic compounds.

3.3.3. Shrimp wastewater treatment results of 2TH-TiO_2 materials

Experiments investigating the ability to treat shrimp farming wastewater by photocatalytic method using 2TH-TiO_2 material are shown in Figure 3.41.

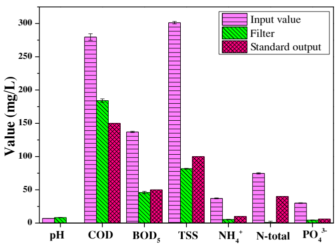

Fig 3.39. Influence of thing test conditions to the treatment results of microorganisms

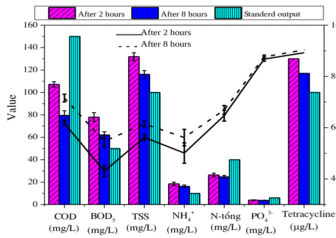

Fig 3.41. Water treatment results Shrimp farming waste of 2TH-material TiO_2 over time

The results show that when the photocatalytic time is extended up to 8 hours, the parameters that reflect the pollution level of the water source are reduced as expected, but the decomposition rate of the pollutants after 8 hours is significantly reduced. with 2-hour process, some indicators such as BOD_5, TSS, NH_4^+, tetracycline still have not met the discharge standards.

3.3.4. The results of wastewater treatment on shrimp farming are based on combining biological methods and photocatalytic methods

The results show that the combination of 2 water treatment methods is as effective as expected, all criteria meet the output effluent standards, in which the values of criteria such as COD, NH_4^+, N-total, PO_4^{3-} drops deeply to reach the allowable value for exhaust. The results show that the practical application of wastewater treatment by combined method before being discharged into the environment is very feasible.

IV.CONCLUSION

1. TiO_2 and 2TH-TiO_2-500 (C, N, S co-doped TiO_2) materials were successfully prepared from Binh Dinh Ilmenite ore by the hydrothermal method without and with the addition of thiourea, respectively. The obtained materials have anatase-type structure, spherical shape with high uniformity and crystallinity.
2. The synthesized 2TH-TiO_2-500 has strong visible light absorption and exhibit higher photocatalytic efficiency than TiO_2 due to the lower recombionation rate of photo-induced electrons and holes, and the narrower bandgap energy. The evaluation of TC photocatalytic degradation indicates that 2TH-TiO_2-500 has a photocatalytic efficiency of 96% after 120 minutes of illumination.
3. After investigating the kinetics of TC, the obtained results show that the photodegradation of TC on 2TH-TiO_2-500 photocatalyst follows the first order kinetic equation of Langmuir-Hinshelwood.
4. The photocatalytic mechanism for TC photodegradation on 2TH-TiO_2-500 photocatalyst was proposed. LC-MS and TOC analyses indicate that the TC photodegradation on the photocatalyst formed many different intermediates before being completely mineralized.
5. The modified TiO_2 materials were successfully employed for the treatment of wastewater from shrimp farms by the biological method in combination with the photocatalytic method. After the treatment,

effluents from shrimp farms meet the standards for discharge into the environment.

V. PAPERS CONCERNING TO THE THESIS

International Journals

1. Nguyen Thi Lan, Vo Hoang Anh, Hoang Duc An, Nguyen Phi Hung, Dao Ngoc Nhiem, Bui Van Thang, Pham Khac Lieu, and Dinh Quang Khieu, "Synthesis of C-N-S-Tridoped TiO_2 from Vietnam Ilmenite Ore and Its Visible Light-Driven-Photocatalytic Activity for Tetracyline Degradation", *Journal of Nanomaterials*, pp. 1-14, Volume 2020, Article ID 1523164.

Vietnam Journals

1. Nguyen Thi Lan, Vo Hoang Anh, Nguyen Thi Viet Kieu, Le Thi Thanh Thuy, Nguyen Phi Hung, "Influence factors of the preparation of TiO_2 nanoparticles from Binh Dinh ilmenite ore using H_2SO_4 agent", Viet Nam journal of catalysis and adsorption, pp. 72-77, 2017.

2. Nguyen Thi Lan, Le Thi Thanh Thuy, Nguyen Thi Viet Kieu, Nguyen Phi Hung, Vo Vien, "Synthesis and modified TiO_2 from Ilmenite Binh Dinh ore by thioure", Journal of Chemistry, Physics and Biology Analysis - vol. 24 , number 1/2019.

3. **Nguyen Thi Lan**, Vo Hoang Anh, Le Thi Cam Nhung, Nguyen Dinh Tuyen, Le Thi Thanh Thuy, Nguyen Phi Hung (7/2019), "Survey of factors affecting photocatalytic ability to decompose tetracycline solution of doped TiO_2 material C, N, S", Journal of Chemistry, 57 (4E1, 2), pp 214-219.

4. **Nguyen Thi Lan,** Vo Hoang Anh, Nguyen Văn Thang, Lê Thị Cam Nhung, Le Thi Thanh Thuy, Nguyen Phi Hung, "Investigate the effect calcination temperature on the ability of photocatalytic decomposition of tetracycline solution by (C, N, S) co-doped TiO_2 materials", *Science Journal of Quy Nhon university*, 2020.