

A - INTRODUCTION

1. Reason for choosing the subject

Recently, we are facing the threat of environmental pollution and infectious disease outbreak caused by emission from industrial zone, plants producing chemical, fertilizer or dye, thermal power plants, food processing plants, etc. that pollutes water, land and air. Solutions to these problems often require enormous cost and may even cause secondary pollution. Therefore, research into the production of effective materials in processing environmental pollutants is very urgent.

Photocatalytic materials are currently being considered as an effective solution to the above problems. TiO_2 is known as an ideal semiconductor for photocatalysis as it is a non-toxic metal oxide with high photochemical activity, low cost, chemical resistance, high refractive index, no photochemical corrosion. At the same time, TiO_2 catalysis happens under normal temperature and pressure, post-reaction catalysts can be recovered and reused easily. The products of the process are CO_2 , H_2O or non-toxic organic compounds. With these advantages, TiO_2 , especially nano TiO_2 , has attracted the attention of scientists in the country and in the world.

However, for TiO_2 catalysts, only ultraviolet radiations corresponding to photons with energy greater than 3.2 eV (band gap energy of titanium dioxide) are absorbed to produce photochemical effects. Therefore, only ultraviolet radiation, which accounts for only about 4% of solar radiation, is effective. In addition, the recombination of photogenerated holes and photogenerated electrons occurs very fast (from 10^{-12} to 10^{-9} seconds), which is also a drawback when deploying photocatalytic systems on the basis of TiO_2 . In order to solve the above problem, we need to produce nanosized TiO_2 with reasonable size and structure, and combine TiO_2 with other components to limit the possibility of recombination of photogenerated holes and photogenerated electrons and enhance photochemical activity in the visible light region.

2. Objectives

The thesis is aimed at creating a catalyst material with high photocatalytic activity which is simply synthesized from available raw materials. The new kind of catalyst material is expected to meet the following requirements:

- High photocatalytic activity, effective treatment of pollutants;
- Simple preparation, from available raw materials, low cost;
- Ability to work efficiently and stably in visible light region;
- Ability to work flexibly in both interrupted and continuous reaction systems, as well as self-cleaning coatings.

3. Scientific and practical meanings

The thesis is aimed at studying the developing photochemical catalysts based on highly active nano TiO₂ which are simply prepared from available raw materials, effective in pollutant treatment and capable of flexible application on interrupted and continuous reaction systems. Specifically:

- Preparation of TiO₂ nanotubes from a variety of materials including commercial TiO₂ which is available on the market by simple hydrothermal methods;
- Combination of TiO₂ nanotubes and materials with photochemical activity in visible light region based on carbon nanotubes (CNTs), ZnO, SiO₂;
- Synthesize TiO₂ sol and apply to the surface of glass material by dip-coating method, using SiO₂ sol-gel.
- Evaluation of photo-oxidation activity of catalysts by using methylene blue as a model reactant;
- Design and manufacture of work equipment in continuous current mode, using sunlight.

4. Innovations and creativities

- The synthesis of TiO₂ nanotubes from commercial TiO₂ by one-step dynamic hydrothermal method has been systematically studied, proposing tube forming mechanisms. This is a simple and effective method that allows the synthesis of TiO₂ nanotubes of uniform quality;
- A complex of catalyst materials has been successfully synthesized based on TiO₂ nanotubes and carbon nanotubes MWCNTs, demonstrating the "synergistic" effect between the two components of MWCNTs and TNTs, reducing the recombination between photogenerated electrons and photogenerated holes;
- The appropriate mass ratio of MWCNTs/TNTs for the MWCNTs/TNTs catalyst system has been determined as 1/1. The catalyst system has a high and stable photochemical activity in the oxidation of H₂S. At the same time,

this catalyst has high sulfur selectivity, reaching 100% in the first 200 minutes of reaction;

- The synthesis of catalyst system based on TiO_2 sol/ SiO_2 by dip-coating method has been systematically studied. The catalyst is highly active, opening the direction for applying photochemical catalysis based on nano- TiO_2 sol on the self-cleaning surface.

5. Thesis's structure

The thesis consists of 148 pages, divided into the following sections: Introduction: 02 pages; Overview: 38 pages; Experimentation: 18 pages; Results and Discussion: 77 pages; Conclusion: 02 pages; Innovations and creativities: 1 page; List of projects that have been published: 01 page; References: 9 pages (including 116 references). The thesis has 12 tables, 93 drawings and graphs.

B - MAIN CONTENTS OF THE THESIS

Chapter 1 - LITERATURE REVIEW

This section provides an overview of TiO_2 -based photochemical catalysis, methods for synthesis of nanomaterials applied to photochemical catalysis on the basis of TiO_2 and denaturing substances, wastewater treatment technologies which focus on wastewater in the laundry detergent industry.

Chapter 2: EXPERIMENTATION

The experimentation was carried out at National keylaboratory for petrochemical and refining technologies

2.1. Synthesis of catalysts

a. Synthesis of TiO_2 nanotubes

Two methods for synthesis of TiO_2 nanotubes have been investigated

- TiO_2 nanoparticles are synthesized from a number of different Ti sources such as $\text{Ti}(\text{OC}_3\text{H}_7)_4$, $\text{Ti}(\text{OC}_4\text{H}_9)_4$, TiCl_4 ; TiO_2 nanotubes are synthesized from TiO_2 nanoparticles.

- TiO_2 nanotubes by one-step synthesis method using commercial TiO_2 particles.

b. Synthesis of TNTs/MWCNTs catalysts

MWCNTs are surface-activated with a mixed solution of HNO_3 : H_2SO_4 before both MWCNTs and commercial TiO_2 are dispersed in 10M NaOH solution (99%, China) with different mass ratios of MWCNTs/TNTs.

c. Synthesis of nano TiO_2 material on carriers

- TNTs/ZnO powders are prepared by directly put TNTs into the synthesis of ZnO-NF/ZnO-TM complex at a varying mass ratio.
- TiO₂/SiO₂ catalysts are synthesized from TiO₂ sol and SiO₂ sol.

2.2. CHEMICAL PHYSICS CHARACTERIZATION

Using XRD, TEM, SEM, BET methods, dynamic light scattering, PL, UV and IR fluorescence to characterize the properties, structure and particle size of catalysts.

2.3. Thape the catalysts

Cylinder formation includes mechanical mixing of binders and catalysts and adding enough water, then tempering the mixture to increase the effect of binders. The tempered mixture is pelleted on the extruder KBV-VV-400-TH of National keylaboratory for petrochemical and refining technologies.

2.3. CATALYTIC ACTIVIY STUDY

Catalytic activity is assessed through the photodegradation of methylene blue (MB) as a model reactant. The methylene blue solution is mixed with distilled water at different concentrations.

After a preliminary investigation with the model, the catalyst is evaluated for activity with actual wastewater. The actual wastewater obtained from a laundry detergent plant contains surfactants, typically linear alkyl sulfonate (LAS) anionic surfactants, which have been pretreated by physical and chemical methods, with COD in the range of 150-250 mg/l.

The organic matter content in wastewater before and after treatment is analyzed by the total organic carbon (TOC) measurement.

Chapter 3: RESULTS AND DISCUSSION

3.1. SYNTHESIS OF TiO₂ NANOTUBES

3.1.1. Effects of raw materials

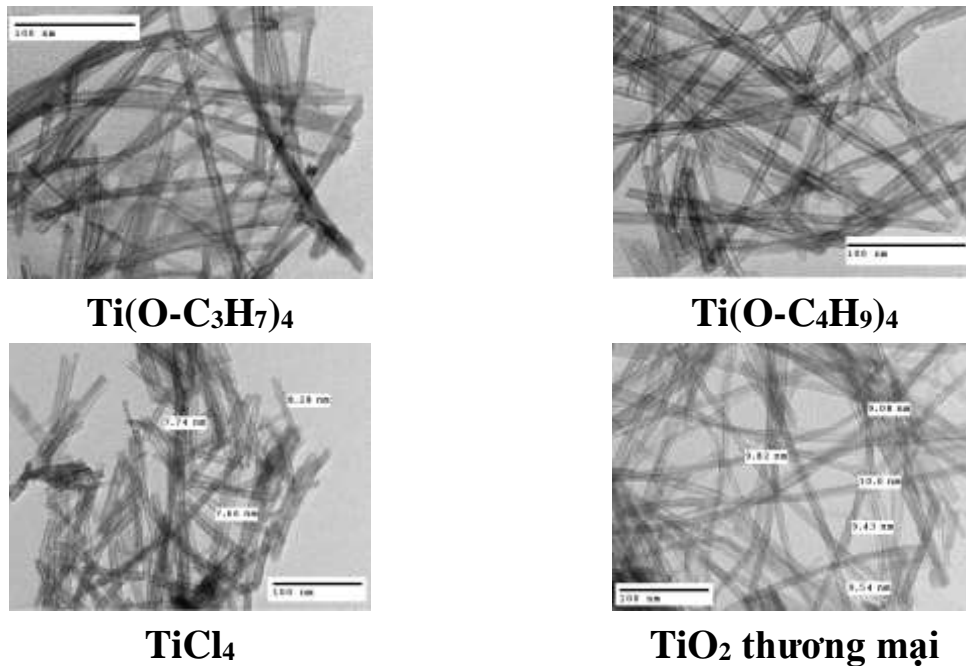
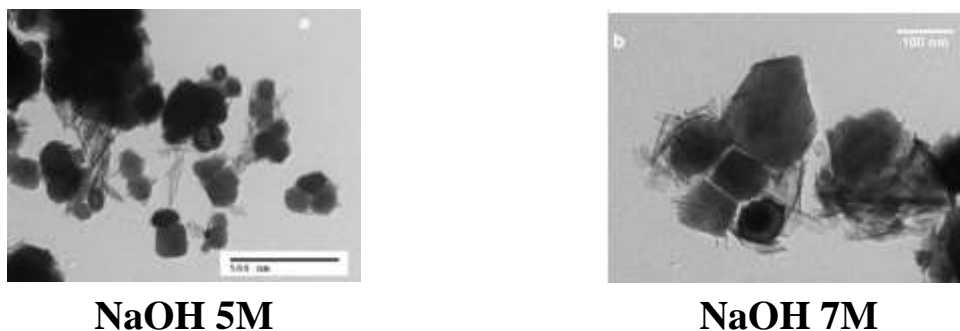
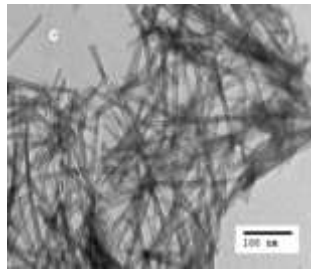


Fig 3.1. TEM images of TiO₂ nanotubes which are fabricated from different materials

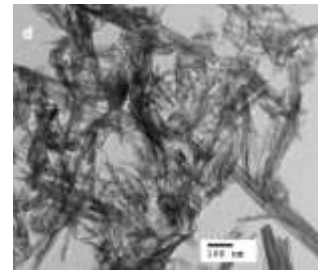
Thus, through the study of effect of raw materials for the synthesis of TNTs. The result showed that, the process of synthesizing TNTs from TiO₂ commercial is the simplest and cheapest. The products TiO₂ get evenly size, high quality equivalent to TiO₂ nanotubes is obtained from other expensive precursors or other method. So, TiO₂ commercial is chose for the next researchs.

3.1.2. Effect of conditions reaction





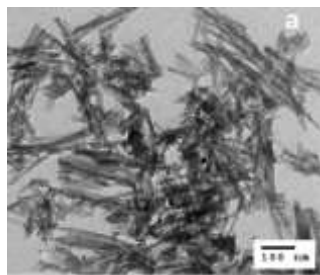
NaOH 10M



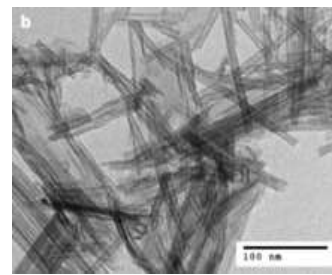
NaOH 15M

Fig 3.2. TEM images of TNTs which is synthesized with different concentration of NaOH

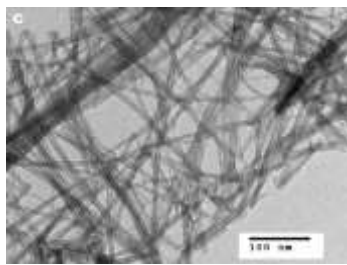
So, 10M is the suitable concentration for synthesis process, will be chose for the next research.



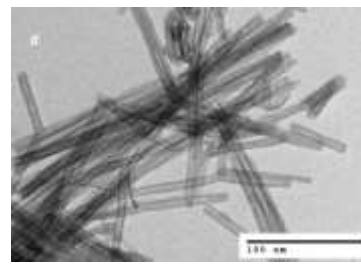
90°C



110°C



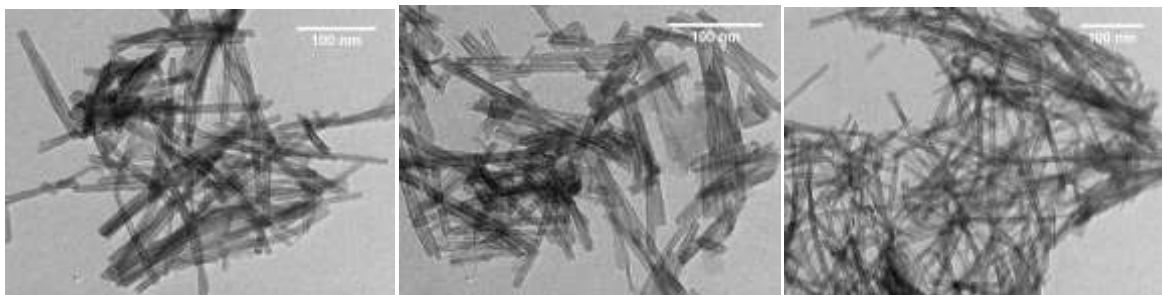
130°C



150°C

Fig 3.3. TEM images of TNTs which are synthesized with different temperature

130°C is the temperature suitable concentration for synthesis process



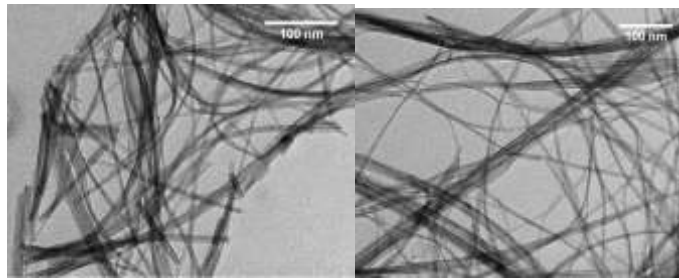


Fig 3.4. TEM images of TNT which are synthesized by different time reaction: (a) 0h; (b) 1h; (c) 3h; (d) 5h và (e) 7h

3h is the reaction time which is suited to concentration for synthesis process.

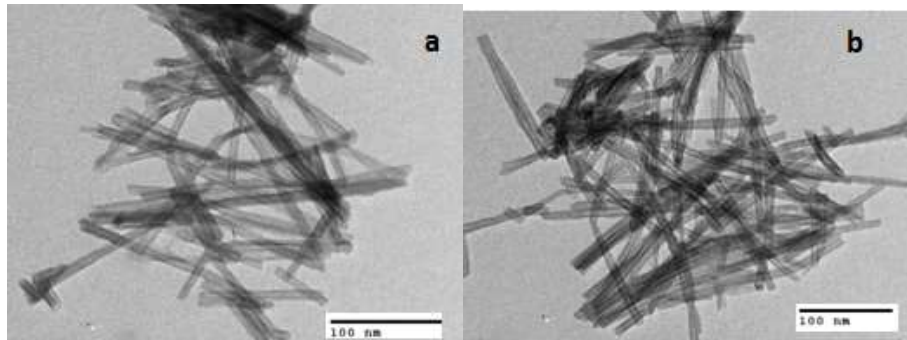


Fig 3.5. TEM images of TNTs before (a) and after (b) treating by acid

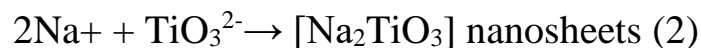
The result showed that, the sample without treat by acid is almost inactive photochemical whereas the sample treat by acid is high photochemical activity. Thus, processing by acid impact significantly on photocatalytic properties of TiO₂ nanotubes.

3.1.3. Formation mechanism of TNTs

Dissolution of TiO₂ precursor:



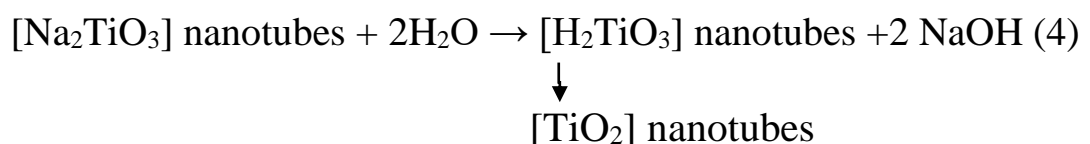
Dissolution–crystallisation of nanosheets



Curving of nanosheets



Washing of nanotubes



3.2. SYNTHESIS OF PHOTOCATALYST BASED ON TiO₂ NANOTUBES

3.2.1. Synthesis of catalysts MWCNTs/TNTs

Table 3.1. Specific area (S_{BET}) of catalysts MWCNTs/ TNTs

Samples	Specific area (S_{BET}), m ² /g
TNTs	311,44
1/10 MWCNTs/TNTs	270,32
1/1 MWCNTs/TNTs	242,31
2/1 MWCNTs/TNTs	188,25
MWCNTs	152,48

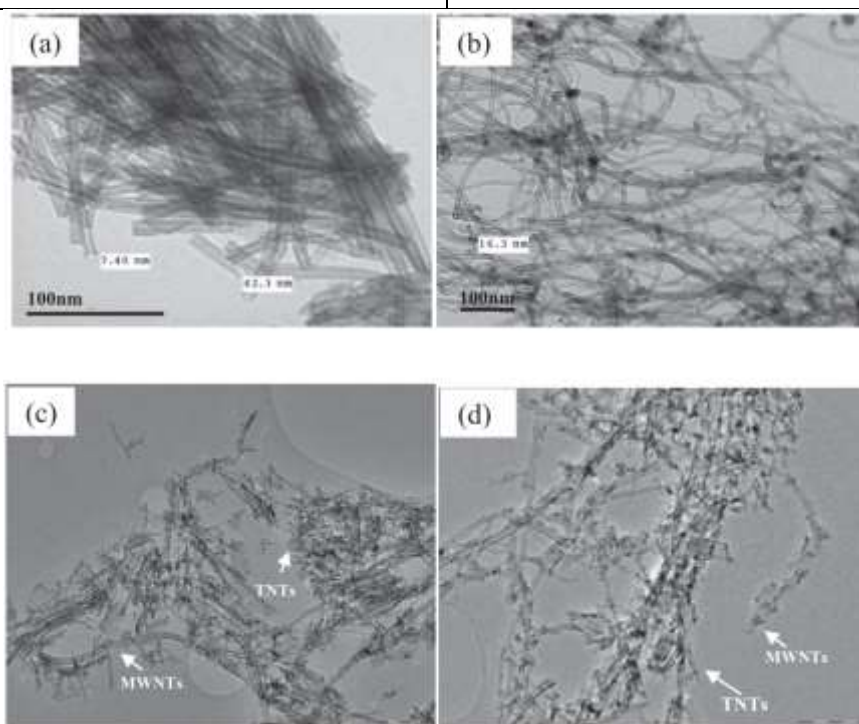


Fig 3.6. TEM images of catalysts MWCNTs/TNTs: (a) TNTs, (b) MWCNTs, (c) 1/10 MWCNTs/TNTs, (d) 1/1 MWCNTs/TNTs,

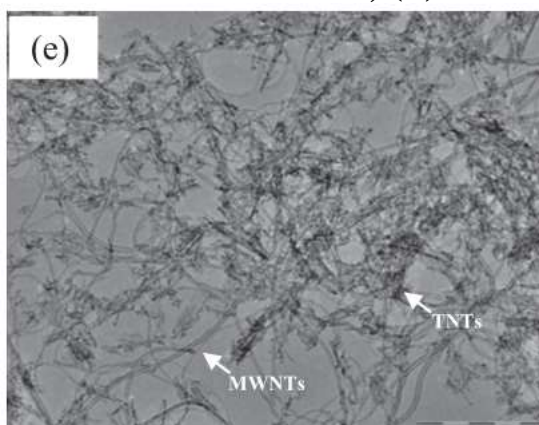


Fig 3.6. (e) 2/1 MWCNTs/TNTs

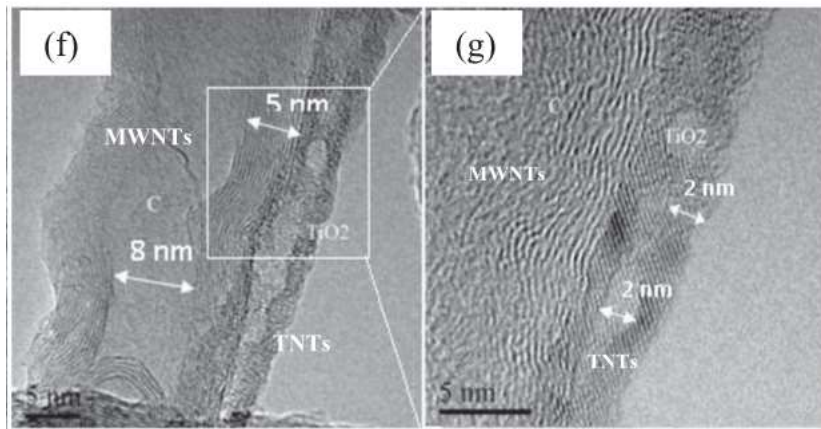


Fig 3.7. HRTEM of catalyst 1/1 MWCNTs/TNTs

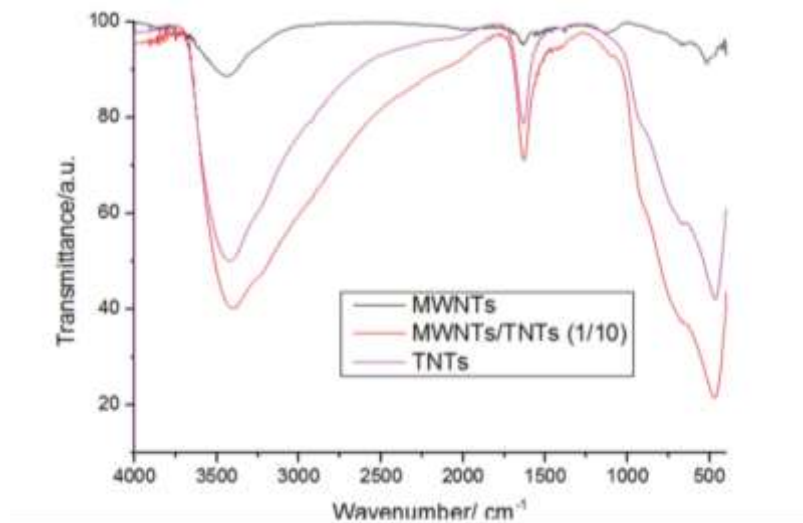


Fig 3.8. FTIR spectra of TNTs, MWCNTs và MWCNTs/TNTs

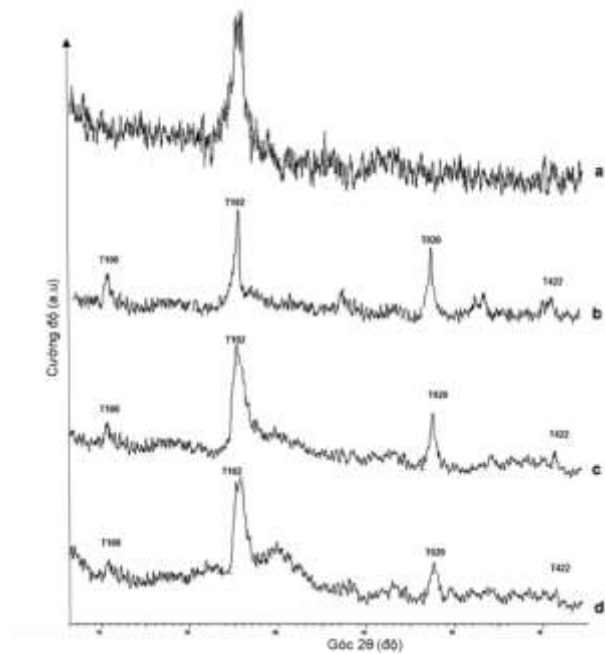


Fig 3.9. XRD patterns of (a) MWCNTs; (b) TNTs; (c) 1/10 MWCNTs/TNTs và (d) 1/1 MWCNTs/TNTs

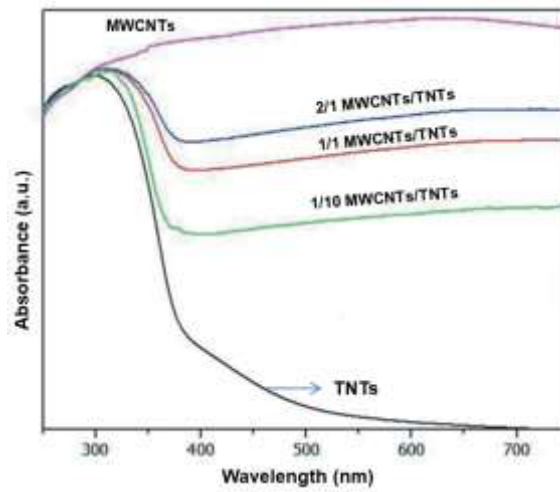


Fig 3.10. UV-VIS-DRS spectra of catalysts MWCNTs/TNTs
Table 3.2. Band-gap values of the synthesized photocatalysts (Kubelka-Munk model)

catalyst	Band gap (eV)
TNTs	3,26
1/10 MWCNTs/TNTs	3,21
1/1 MWCNTs/TNTs	3,08
2/1 MWCNTs/TNTs	3,05
MWCNTs	-

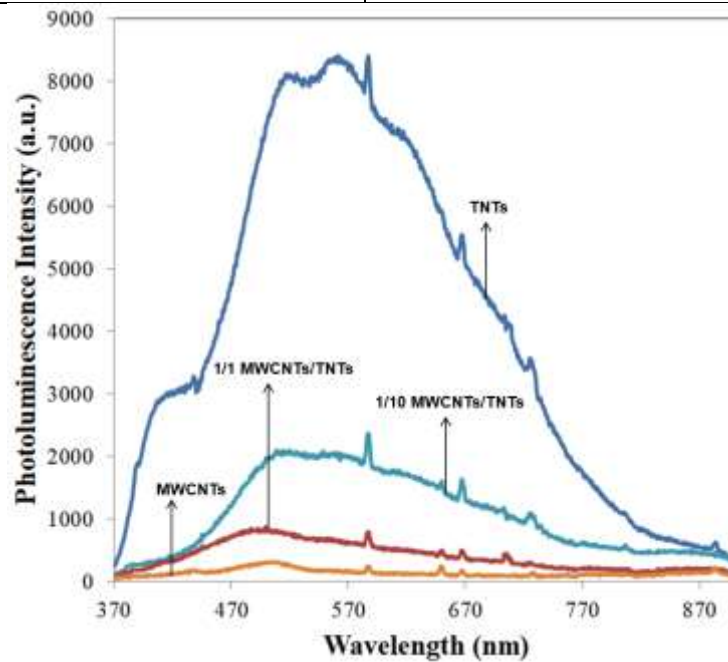


Fig 3.11. PL spectra of catalysts MWCNTs/TNTs

3.2.2. Synthesis of TNTs/ZnO

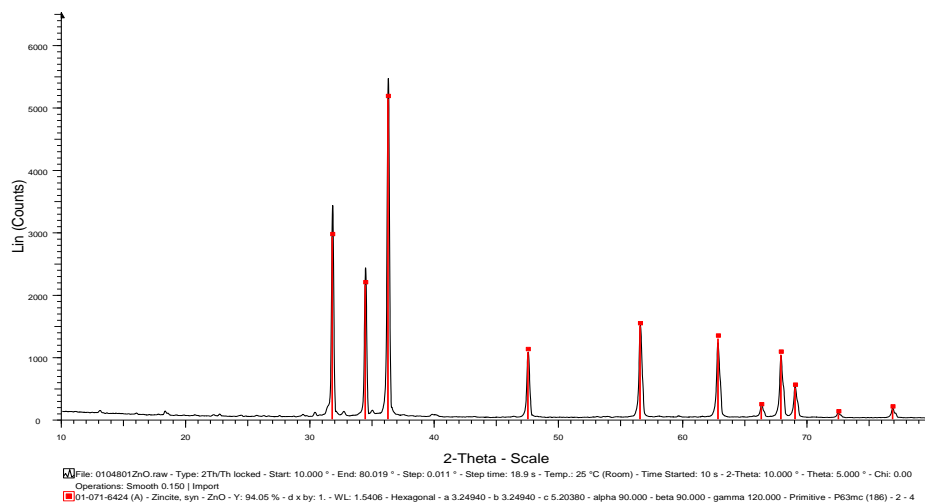


Fig 3.12. XRD patterns of ZnO

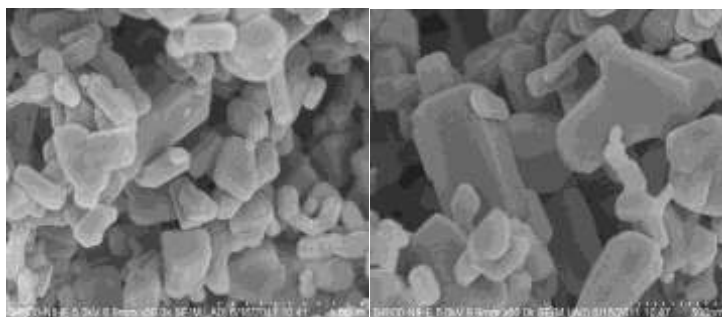
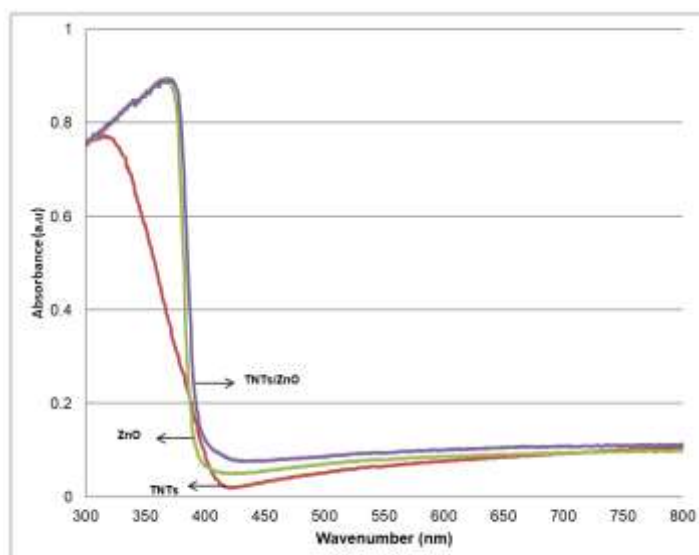


Fig 3.13. SEM images of ZnO



Hình 3.14. UV-Vis spectra of TiO₂/ZnO

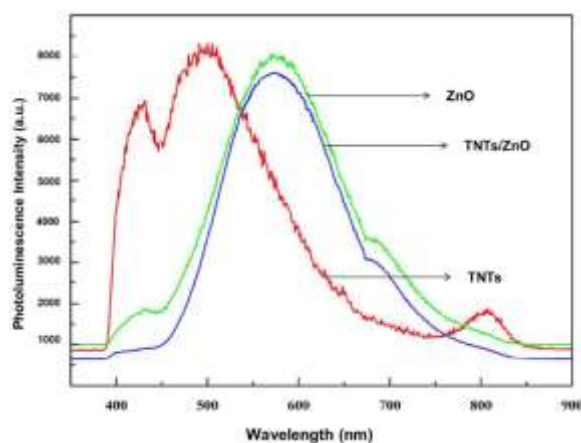


Fig 3.15. PL spectra of catalysts TNTs, TNTs/ZnO và ZnO
Table 3.3. Effect of ZnO content in nanocomposite TNTs/ZnO

STT	ZnO content in TNTs/ZnO	conversion MB after 30 min (%)
1	100	55
2	0	85
3	90	89
4	80	89
5	70	89

Shape the catalyst TNTs/ZnO

Inherited other researchers, pseudo-boehmit is chose such as binder for shaping catalysts TNTs/ZnO with 12% weight content. The results showed that pellet TNTs/ZnO has the specific surface area 108,5 m²/g; Mechanical robustness reached 50 N/cm². Catalyst has high mechanical robustness because attendance of pseudo-boehmit and ZnO-NF/ZnO-TM such as good binders

Mechanical robustness measure results of catalyst after dipping few days in water is showed in Tab. 3.4.

Table 3.4 . Mechanical robustness measure results of catalyst

Time (day)	Mechanical robustness (N/cm ²)
0	50,00
4	48,93
10	45,33
20	43,05
30	39,77

Results of photocatalytic activity test in MB degradation reaction showed that the catalysts has high activity photochemical with 95,3% to 97,2% in 50 min reaction.

3.2.3. Synthesis of TiO_2/SiO_2

The combination of TiO_2 and SiO_2 not only enhances TiO_2 photochemical activity, but also enhances the physical properties of the catalyst such as Mechanical robustness, transparent.

a. Synthesis of sol silica

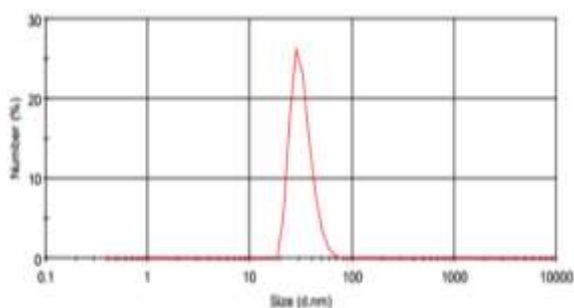


Fig 3.16. Partical size of sol silica: [Si]=0,4M, pH=8, Temperature: 60°C

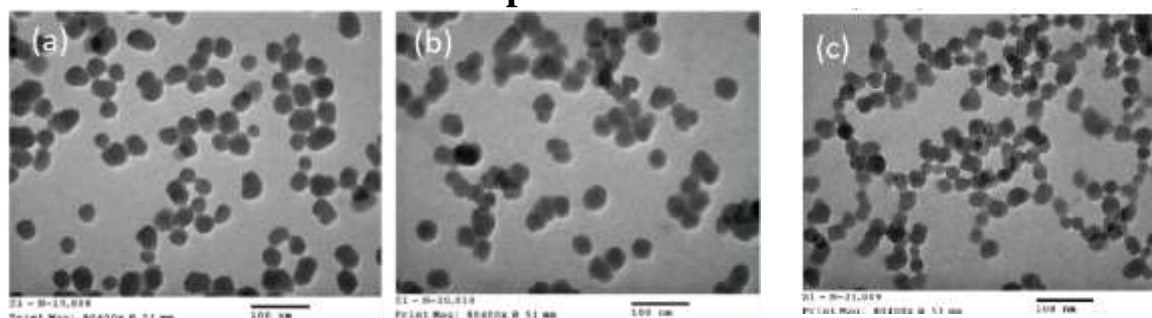
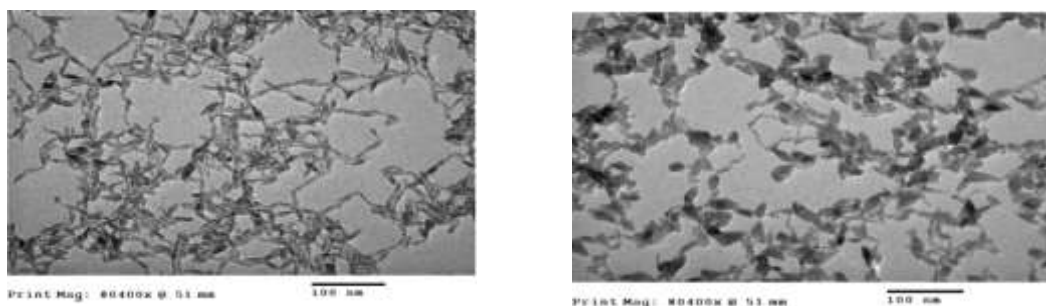


Fig 3.17. TEM image of sol silica when: (a) without surfactant, (b) PEG 1000, (c) PVP K30

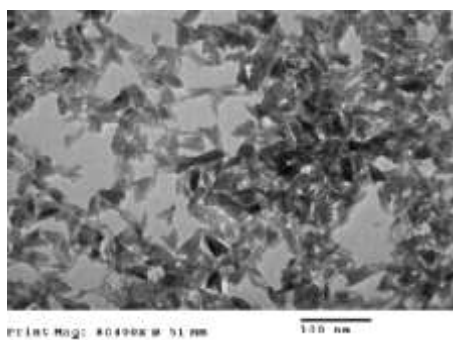
b. Synthesis of sol TiO_2

Morphology and structure of partical in sol TiO_2 are illustrated in fig. 3.18.



(a) Sample C% TiO_2 =0,6%

(b) Sample C% TiO_2 =0,7%



(c) Sample $C\%_{TiO_2}=0,8\%$

Fig. 3.18. Morphology and structure of partical in sol TiO_2 : **a - 0,6%**; **b - 0,7%**; **c - 0,8%**

Concentration 0,7% is chose for the next research

Table 3.5. Effect of pH of gel $Ti(OH)_4$ to end product

pH	End products	pH	End products
3	No gel	7	Sol, transparent
4	Gel, yellow, transparent	8	Sol, transparent (stable)
5	Gel, yellow, transparent	9	Sol, transparent
6	Gel, yellow, transparent	10	Sol, transparent

Thus, pH= 8 is chose for the next research.

Sol TiO_2 which is synthesized at those suitable conditions, is evaluated photocatalytic activity in photooxidation MB reaction under radiation solar, the results were showed in fig. 3.59.

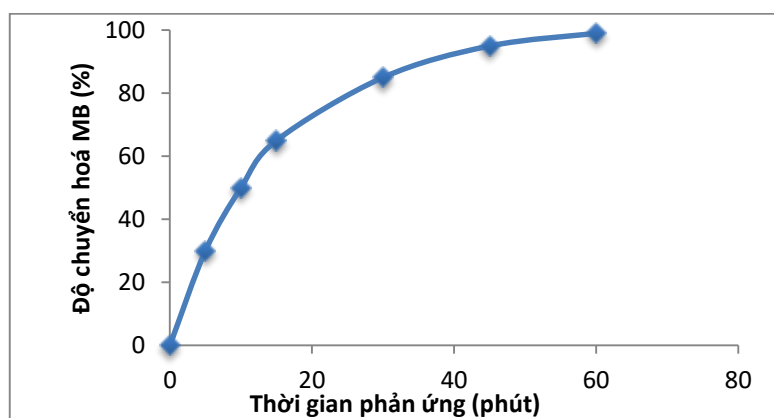
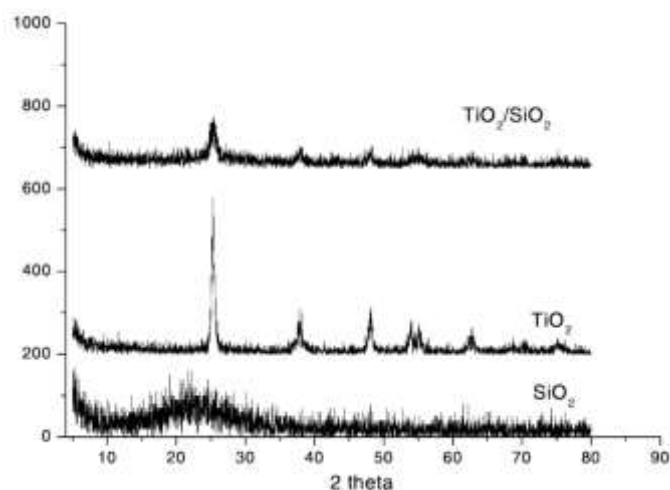


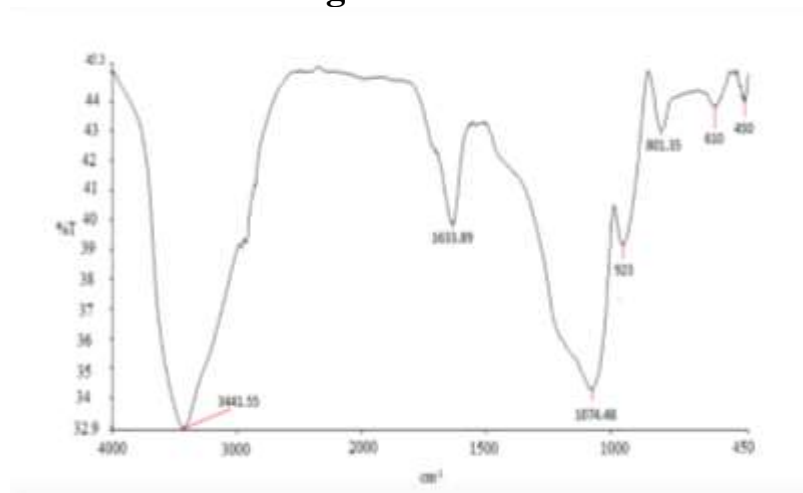
Fig. 3.19. Photocatalytic activity of coating TiO_2

The results from fig. 3.19 showed that, coating TiO_2 can degraded 70% methylene Blue in 20 minutes and degraded completely MB in 1 hour (conversion 99%).

Catalyst $\text{TiO}_2/\text{SiO}_2$ was fabricated on substrate which is glass rod with 100mm x 20mm x 2mm by dip-coating method. XRD patterns of SiO_2 , TiO_2 , and catalyst $\text{TiO}_2/\text{SiO}_2$ after calcinating at 500°C in 30 min were showed in fig. 3.20.



Hình 3.20. XRD patterns of SiO_2 , TiO_2 , and $\text{TiO}_2/\text{SiO}_2$ after calcinating at 500°C in 1 hour



Hình 3.21. FTIR spectra of $\text{TiO}_2/\text{SiO}_2$ is recorded at $4.000 - 450 \text{ cm}^{-1}$

FTIR spectra of $\text{TiO}_2/\text{SiO}_2$ given full information about bonds of components in nanocomposite catalyst. In other words, TiO_2 have fixed successfully on substrate SiO_2 .

Photocatalytic activity of catalyst $\text{TiO}_2/\text{SiO}_2$ is showed in fig.3.22

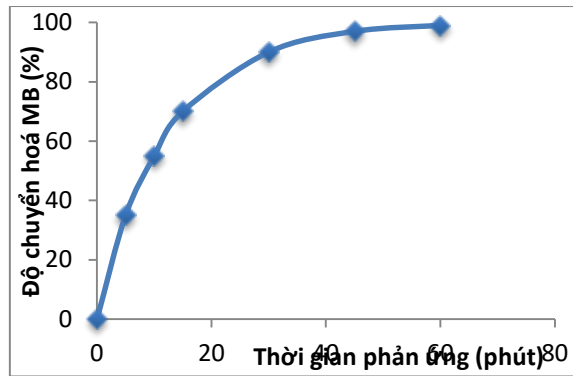
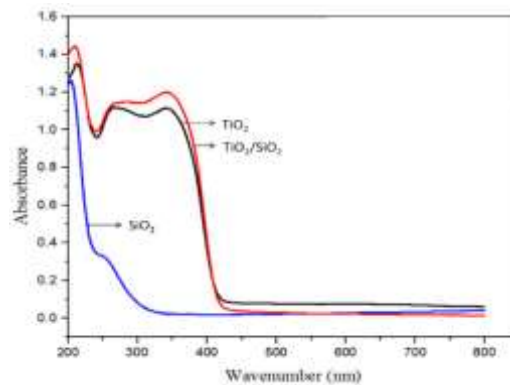


Fig 3.22. Photocatalytic activity of catalyst TiO₂/SiO₂

The results showed that, MB is almost degraded completely in 60 minutes. That means, The results showed that, MB is almost degraded completely in 60 minutes. That means, SiO₂ attendance in catalyst TiO₂/SiO₂ that improved partly photocatalytic activity of catalyst.

The results are completely suitable with UV-Vis spectra of TiO₂/SiO₂ that were illustrated in Fig. 3.23.



Hình 3.23. UV- Vis spectra of catalyst TiO₂/SiO₂

UV- Vis spectra of TiO₂/SiO₂ showed that the combination of TiO₂ and SiO₂ caused wide-open of absorb solar radiation which tend absorb of red radiation.

3.2.4. Synthesis of sol TiO₂-SiO₂

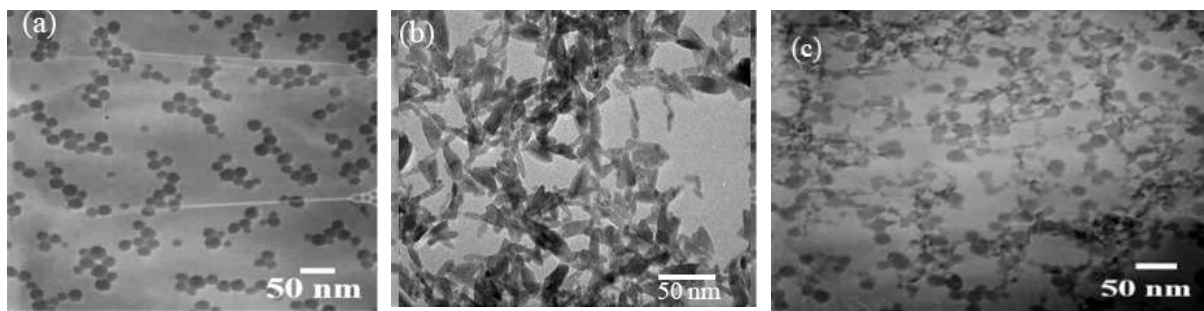


Fig. 3.24. TEM images of sol: (a) sol SiO₂, (b) sol TiO₂, (c) sol SiO₂-TiO₂

Results of photocatalytic activity of $\text{SiO}_2\text{-TiO}_2$ test in MB degradation reaction were illustrated in Fig. 3.25.

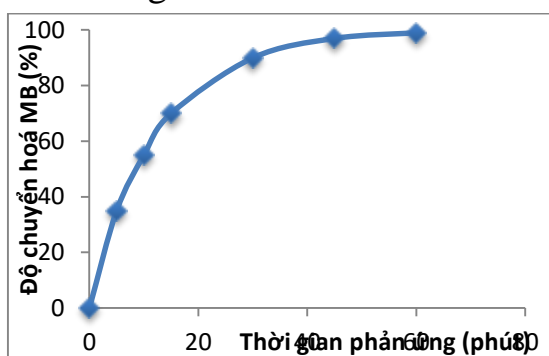


Fig. 3.25. Photocatalytic activity of sol $\text{TiO}_2\text{-SiO}_2$

The result from fig.3.25 showed that, $\text{TiO}_2\text{-SiO}_2$ coating can degraded 70% methylene Blue in 20 minutes and degraded completely MB in 1 hour (conversion 99%).

3.3. EVALUATE CATALYTIC ACTIVITY OF CATALYSTS

3.3.1. Evaluation of photocatalytic activity on photodegradation Methylene blue reaction

Photocatalytic activity of catalysts MWCNTs, MWCNTs/TNTs, TNTs, và TNTs/ZnO have evaluated by photodegradation reaction of methylene blue (batch model). The results showed in fig. 3.26

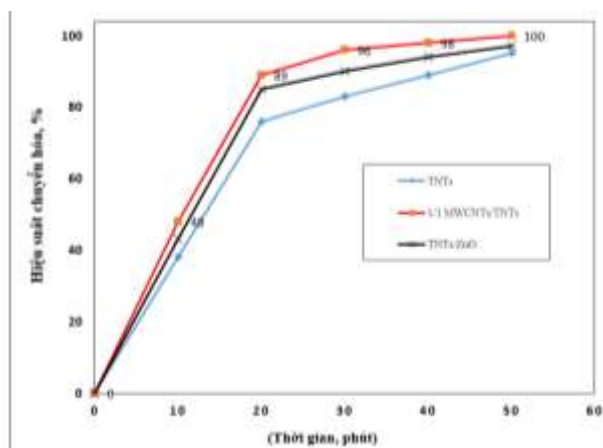


Fig. 3.26. Photocatalytic activity of catalysts

Photocatalytic activity of TNTs has great performance when it's combined with MWCNT or ZnO. Especially, catalyst MWCNTs/TNTs 1:1 can degraded MB 90% in 20 min. The results showed again, the combination of TNTs and MWCNTs is very effective. It can be applied in catalytic and environment field.

3.3.2. Investigation of photocatalytic activity of MWCNTs/TNTs 1/1 in photooxidation H₂S reaction.

The conversion and selectivity of H₂S were recorded when it was test on catalyst 1/1 MWCNTs/TNTs in oxidation H₂S reaction . The results were compared wiht catalyst TNTs. The comparison results were shown on fig. 2.27

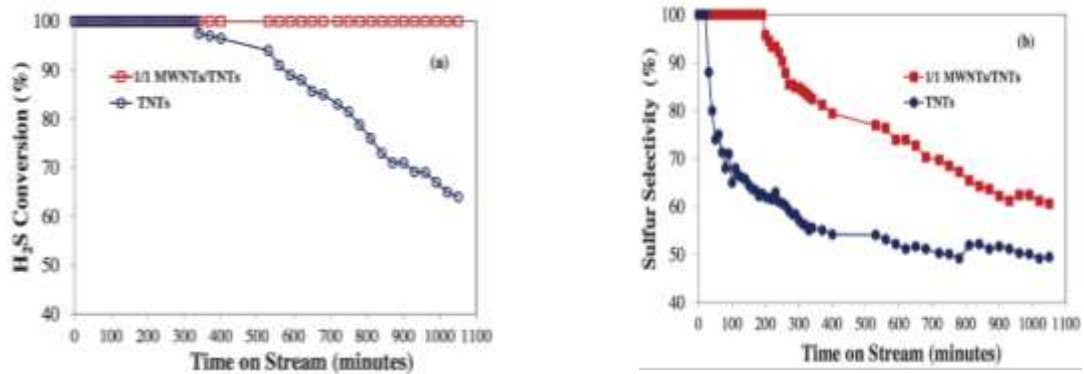


Fig. 3.27. Conversion and selectivity of photooxydation H₂S reaction on catalyst 1/1 MWCNTs/TNTs and TNTs

The conversion of H₂S and selectivity of sulfur were shown on fig. 3.28 and fig. 3.29.

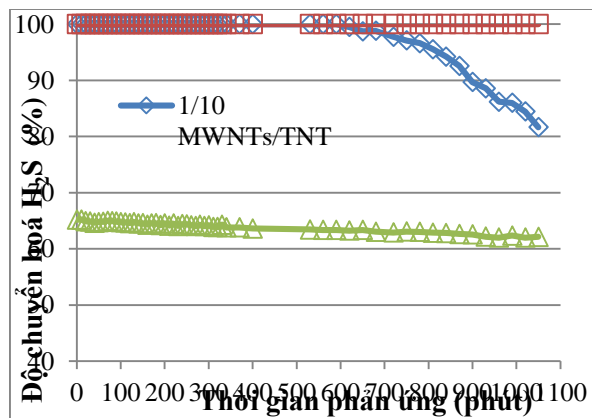


Fig. 3.28. Conversion of H₂S

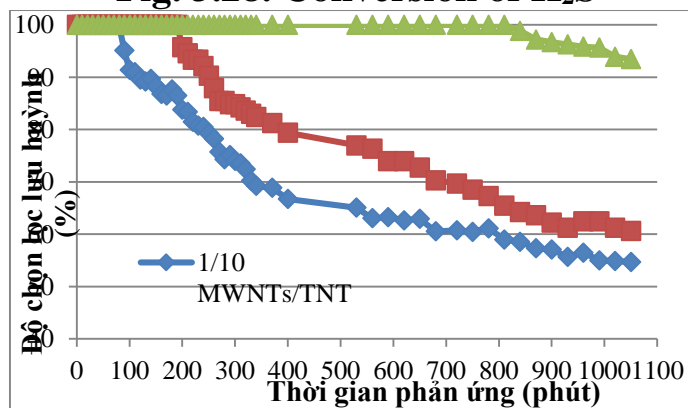


Fig. 3.29. Selectivity of sulfur

Thus, catalyst MWCNTs/TNTs with ratio MWCNTs/TNTs = 1/1 were show more stable performance than the others catalyst.

3.4. STUDY ON PHOTOCATALYTIC DEGRADATION OF MB BY CATALYST TNTs/ZnO USING CONTINUOUS-FLOW REACTION SYSTEM

3.4.1. Effect of reaction time

The results were showed in fig.3.30. The conversion reached 100% when flow-rate below 6.300 mL/h.

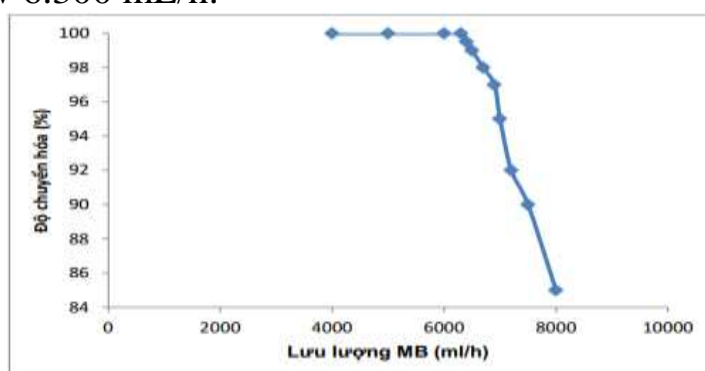


Fig. 3.30. Effect of flow-rate

3.4.2. Effect of temperature

The results showed that, the conversion wasn't almost changed then temperature changed from 20 to 40°C.

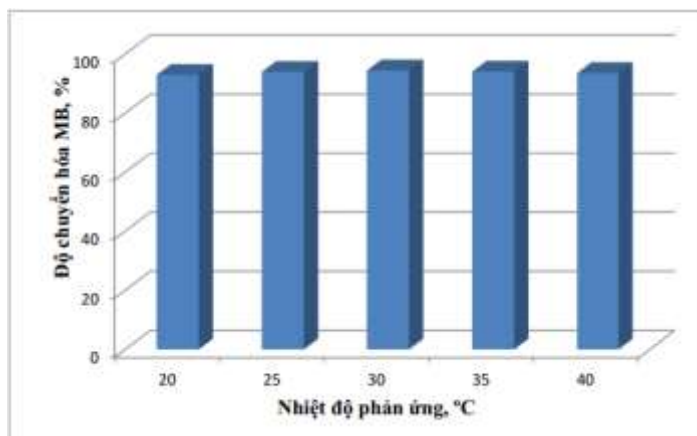


Fig. 3.31. Conversion of MB at different temperatures

3.4.3. Effect of pH

The results on Fig.3.32 showed that, the conversion reached max at pH=7.

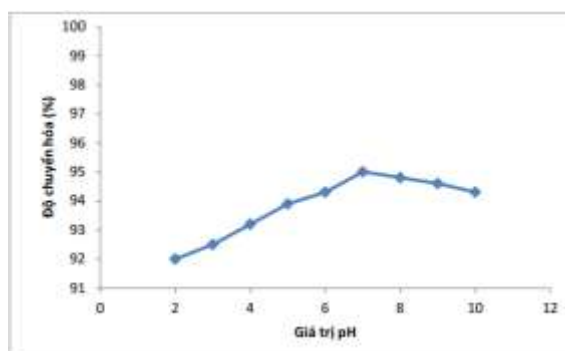


Fig. 3.32. Effect of pH value

3.4.4. Evaluate durability of catalyst

The result showed that, photocatalytic activity of catalyst was durability in long time. After 30 days, the conversion of MB was only decreased 4%. Thus, catalyst is almost durability phototcatalytic activity.

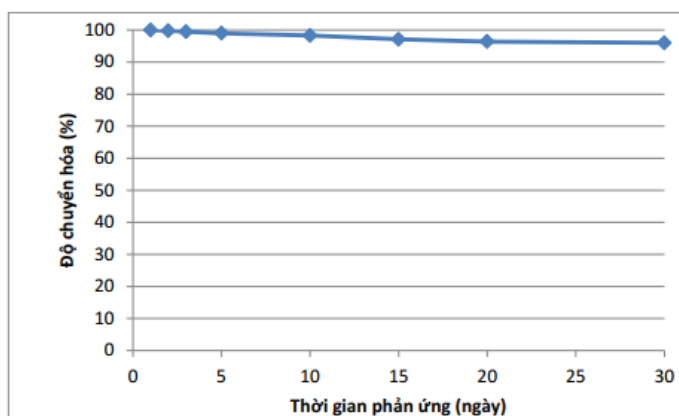


Fig. 3.33. conversion of MB in 30 days

3.4.5. Research on catalyst regeneration method

Water was went through the catalyst with same flow-rate of MB 6300 ml/h. Turn on the lamb to regenerate catalyst. The results were showed in fig. 3.34.

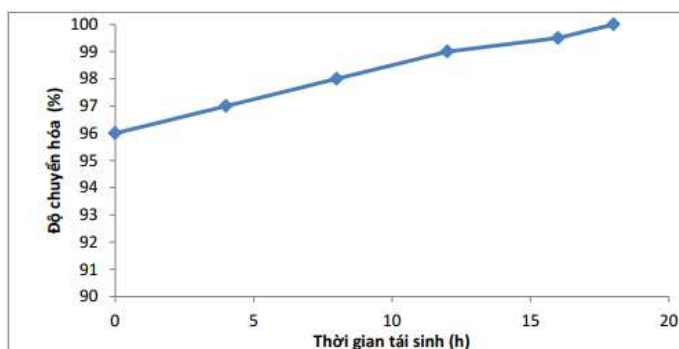


Fig 3.34. Effect of time regeneration of catalyst

3.5. SUTY ON PHOTOCATALYTIC DEGRADATION OF WASTE WATER CONTAIN SURFACTANTS USING CONTINOUS-FLOW REACTION SYSTEM

Table 3.6. Specifications of waste water which contain organic compound before treating by photochemical process

STT	Specifications	Unit	Result
3	COD	mg/l	207
4	TOC	mg/l	52,6

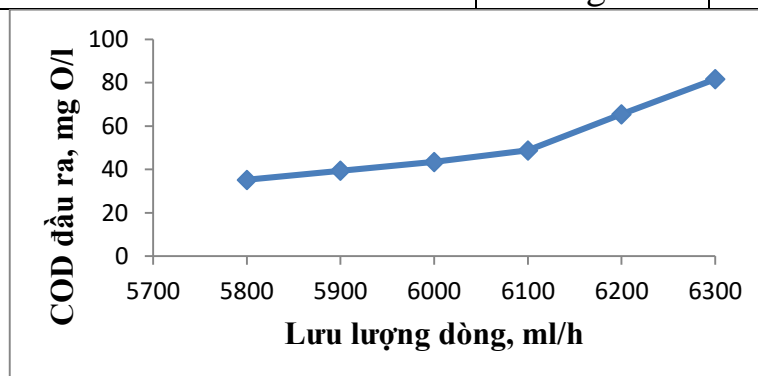


Fig 3.35. Effect of flow-rate to index COD

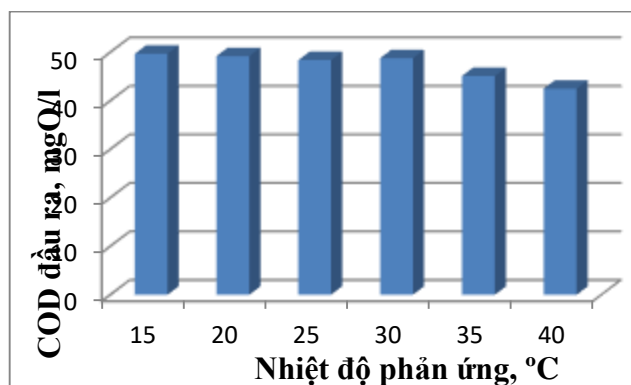


Fig 3.36. Index COD at different temperature

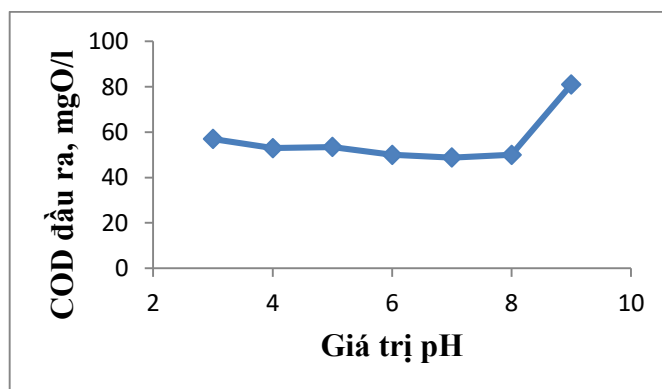


Fig. 3.37. Effect of pH to index COD of water

**Table 3.7. Specifications of water after treating
by photochemical process**

No	Specifiations	Results
2	TOC, mg/l	12,6
3	COD,mg/l	48,8

The results on table 3.7 showed that, total organic chemical in water after treating by photochemical process were decreased significantly from 52,6 mg/l to 12,6 mg/l that means 76% of organic chemical were reduced by photochemical process, using catalyst TNTs/ZnO. In other words, catalyst TNTs/ZnO can degraded efficaciously organic chemicals in waste water which contain surfactants.

CONCLUSION

- Have studied the synthesis, characterization of physicochemical and photochemical properties of 6 photochemical catalyst systems based on synthesized TiO₂, including: TNTs, TNTs/MWCNTs, TNTs/ZnO, TiO₂ sol, TiO₂/SiO₂, TiO₂-SiO₂. In particular, the synthesis of TiO₂ nanotubes from commercial TiO₂ by one-step dynamic hydrothermal method has been systematically studied, mechanisms of tube formation have been proposed. This is a simple and efficient method that allows the synthesis of high and uniform quality uniform TiO₂ nanotubes (with a diameter of about 10 nm, specific surface area of 280 m²/g).
- The "synergistic" effect between the two components of MWCNTs and TiO₂ nanotubes in MWCNTs/TNTs catalysis has been demonstrated, contributing to increased catalytic activity compared to the activity of individual components. The most appropriate mass ratio of MWCNTs/TNTs has been determined as 1/1. In the complex of MWCNTs/TNTs, TNTs (with an average wall thickness of about 2 nm) are dispersed and attached to the walls of MWCNTs (5 nm thick) uniformly. Results of studying the photo-oxidation activity of H₂S on MWCNTs/TNTs catalyst showed that the catalyst obtained has high and stable photochemical activity for a long time (1,000 mins). At the same time, this catalyst has high sulfur selectivity, reaching 100% in the first 200 minutes of reaction;
- The synthesis of nano TiO₂ sol from TiCl₄ has been systematically studied and appropriate reaction conditions have been determined. TiO₂ sol with a particle size of 12 nm, the shape of "rice grain" and good dispersion is synthesized under TiO₂ content condition of 0.7%; pH = 8; temperature: 97°C; time: 30 hours. Catalysts based on TiO₂ sol are prepared by solubilizing TiO₂ onto the glass substrate shown to be active in the photo-oxidation of methylene blue under sunlight. This result showed that the obtained TiO₂ sol can be effectively applied as a self-cleaning coating by simple coating method without heat treatment;

- Suitable reaction conditions for synthesis of sol nano SiO₂ from TEOS have been determined. Sol SiO₂ which has a particle size of 23 nm is well dispersed and synthesized at [Si] = 0.4M, reaction temperature: 60°C, pH = 8.
- The parameters that affect the activity of photo-oxidation catalysts based on ZnO/TNTs have been systematically studied, on a continuous catalytic reactor system, the catalysts are able to remove LAS in wastewater up to 76%.

LIST OF PUBLICATION

1. Synthesis of titanium dioxide nanotubes via one-step dynamic hydrothermal process; Journal of Materials Science; Volume 49, Issue 16, pp 5617-5625 (2014).
2. Synthesis of carbon nanotube/titanate nanotube composites with photocatalytic activity for H₂S oxidation; Journal of Sulfur Chemistry, Vol 38, Issue 3, pp 264-278 (2017).
3. Study on effect of factors to the particle size in the nanosilica synthesizing process, Viet Nam Journal of Chemistry and Applications, No 3(43)/2018, 16-10
4. Viet Nam Journal of Chemistry and Applications, Viet Nam Journal of Chemistry and Applications, 7 issue 2, 2018, 31-36