Preparation of Ag modified ZnO composites and their photocatalytic activity

Rattapong Umpriwan

Supakit Wattanarungsan

Thampon Sukhasem

Mahidol Wittayanusorn School

Thailand

Water is life, 5-11 June 2016, Maurick College, The Netherlands

ABSTRACT

Preparation of Ag modified ZnO composites and their photocatalytic activity

Rattapong Umpriwan, Supakit Wattanarungsan, Thampon Sukhasem, Sorachai Sae-lim[1] and Cheewita Suwanchawalit[2]

[1]*Department of Chemistry, Mahidol Wittayanusorn School, Nakhon Pathom, 73170, Thailand*

[2]*Department of Chemistry, Faculty of Science, Silpakorn University, Nakhon Pathom, 73000, Thailand*

Zinc oxide (ZnO) has attracted wide interest because of its good photocatalytic activity, high stability, antibacterial property and non-toxicity. The objective of this research is to study the photocatalytic activity of Ag doped ZnO for degradation of methylene blue dye in aqueous solution under visible light irradiation. The project has studied the effect of Ag dopant concentrations (5, 10, 25, 50 mmol) on the preparation of Ag doped ZnO synthesized via a sample precipitation method using zinc oxide and silver nitrate as precursors and sodium hydroxide as a precipitating agent. The prepared samples were characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), and Fourier transform infrared spectroscopy (FTIR). The degradation of methylene blue ($1.0x10^{-5}$ M) dye in aqueous solution was evaluated under visible light irradiation. The results indicated that the powdered of 50 mmol Ag dopant and pH=10 were highest photocatalytic efficiency.

ACKNOWLEDGEMENT

We wish to express our deepest and sincere gratitude to my advisor, Sorachai Sae-lim, for his valuable instructions, expert guidance and excellent suggestions. Special thanks are addressed to Dr. Cheewita Suwanchawalit, Department of Chemistry, Faculty of Science, Silpakorn University, Nakhon Pathom, Thailand, for her guidance.

This material support involved in this study was partly supported by Department of Chemistry, Mahidol Wittayanusorn School.

We would also like to express our appreciation to the staffs of the Department of Chemistry, Mahidol Wittayanusorn School for making this thesis possible.

Finally, none of this would have been possible without the love and encouragement of our family and friends. We thank them all for their kindness and valuable advice. All effort undertaken to complete this thesis will always be kept in our mind.

15 February 2016

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Chapter 1
INTRODUCTION

1.1 Statement of the problem

Water is a basic requirement in all industrial processes ; domestic and commercial activities, so wastewater generated from different activities contains various contaminants which are harmful for both flora and fauna existing on this planet. The industrial operations mainly pharmaceutical, textile, pesticides and other organic chemical manufacturing industries generate waste water that contains phenolic compounds and various dyes. These effluents are intensely colored and are contaminated with high concentration of organic compounds such as suspended and dissolved salts and many other recalcitrant compounds. Even small concentration of these compounds present in effluent causes toxicity and fouls water odors. If these effluents are improperly treated, they will pose a serious threat to all aquatic species because hydrolysis of the pollutants in waste water can produce a great deal of toxic products. Degradation of these non-biodegradable organic compounds is not possible by conventional biological treatment processes, so there has been a lot of interest in the application of the advanced oxidation processes (AOP's) for the removal of such organic compounds. Many processes such as photolysis, photocatalytic oxidation, ozonation, Fenton oxidation, wet air oxidation and membrane separation have been proposed for the degradation of these compounds to an even lower concentration level.

Textile wastewater processing is one of the most important industries in the world and it employs a variety of chemicals, depending on the nature of the raw materials and products. Main pollution in textile wastewater comes from dyeing and finishing processes. These processes require the input of a wide range of chemicals and dyestuffs, which generally are organic compounds of complex structures. However, because not all of them are contained in the final product, its waste has caused some disposal problems. Major pollutants in textile wastewaters are high suspended solids, chemical oxygen demand, heat, color, acidity, and other soluble substances. The removal of color from the wastewaters of textile industry and dyestuff manufacturing industry represent a major environmental concern. In addition, only 47% of 87 dyestuffs are biodegradable. It has been documented that residual color is usually due to insoluble dyes which have low biodegradability. So textile wastewaters is an environmental challenge for the textile industry, not only as liquid waste but also in its chemical composition (*Venceslau et al., 1994*). If these effluents are improperly treated, they will pose bad threats to all species on earth because the hydrolysis of the pollutants in the wastewater can produce a great deal of toxic products (*Jun Wang et. al 2005*).

The textile industry is facing tremendous competition, which has resulted in the use of, large amount of chemicals, as well as dyes, and releasing them into water sources. Unless the wat to decrease the amount of dyes are found, damages to the environment and unpleasant sceneries will persist. Even though most industries are using various methods to reduce the amount of chemical wastes in their industrial-wastewater, the colour caused by dyes is a significant problem that remains complicated to solve. In 1996, the Thai Ministry of Industry announced the need to address the dangers posed by the remaining dyes in water sources.

Photocatalytic oxidation is a process to degrade chemicals using light as a catalyst. Photocatalytic oxidation process uses energy from UV-light and the catalyst which is semiconductor. When a particle of light that has more energy than an energy band in a chemical (Eg) which is at the surface of semiconductor, electron(e-cb) will be excited from the valance band (VB) into the conducted band (CB) and it will make a hole(h+vb). E-cb reacts with molecules of oxygen and provides superoxide ion radicals while H+vb receives the electron from the organic molecules directly and changes the hydroxyl-ion to the hydroxyl radicals (OH·) (Usaporn ;Mahmoodi et al. 2006; Kuo and Ho 2001) which is an oxidizer that can degrade the organic compounds in the solution. Based on our project, ZnO/Ag is used to be the Photocatalyst. ZnO which is doped by Ag in order to hold the electrons in the conduction band and to reduce band gap energy which increases the redshift process of the Absorption band from the frequency of Ultraviolet to the frequency of visible light (Mu-Hsiang Hsu ,Chi-Jung Chang. 2014: 5). We also formed ZnO/Ag on proper materials in order to make is recyclable, lower the cost of water treatment, and increase the efficiency of water treatment processes.

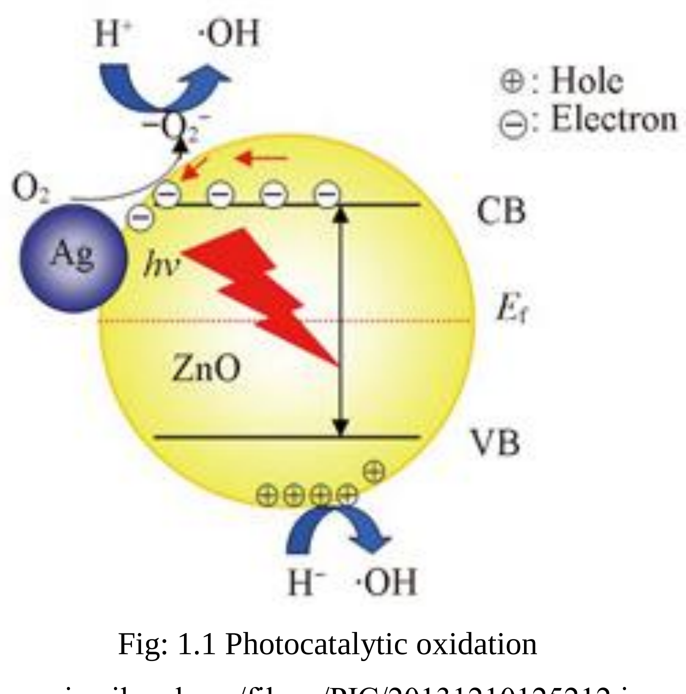

Fig: 1.1 Photocatalytic oxidation

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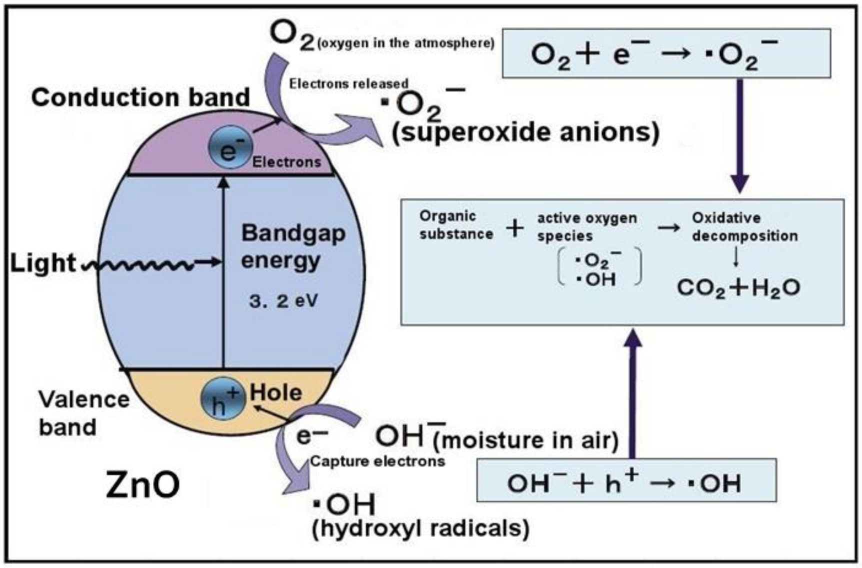


Fig: 1.2 Photocatalytic oxidation of ZnO

1.2 Objectives

1. To synthesize ZnO/Ag and find the most proper condition that can mostly degrade methylene blue.

2. To form ZnO/Ag on rubber sheet and provide recyclable ability.

1.3 Scope of study

The efficiency of ZnO/Ag is only tested with methylene blue.

1.4 Research venue

Department of Chemistry, Faculty of Science Silpakorn University.

Department of Chemistry, Mahidol Wittayanusorn School.

1.5 Expected profit (benefits)

1. Found the best condition, including pH and concentration, to synthesize ZnO/Ag.
2. Made the most efficient ZnO/Ag to be a catalyst in the photocatalytic process.
3. ZnO/Ag can be reused.

Chapter 2

Methodology

As described in this chapter,materials and methods used during this research, include chemicals, glassware instruments like the UV photo reactor, UV-Vis Spectrophotometer for pH adjustment and analysis, Electrical conductivity (EC) measurement, and procedures used in treating dyes and effluent solutions with the UV/ZnO catalysis and UV/ZnO/Ag. The compilation of the solutions at varied pH, ZnO dosages and varied UV contact times for the Methylene blue dyes at varied amount.

2.1 Materials

2.1.1 Fluorescent lamp 20w

2.1.2 UV-light lamp 20w

2.1.3 Magnetic stir

2.1.4 500 ml-Beaker

2.1.5 250 ml-Beaker

2.1.6 Dropper

2.1.7 Test tube

2.1.8 UV-vis spectrometer

2.1.9 Vacuum-filter

2.2 Chemicals

2.2.1 ZnO

2.2.2 $AgNO_3$

2.2.3 NaOH

2.2.4 Methylene blue

2.2.5 Glucose solution

2.2.7 Rubber compound

2.2.7 Ammonia solution

2.3 Dye

A Dye sample (Methylene blue) was collected from textile industries which is used as basic coloring agent in the industry. The dye was used without further purification. A full scan of dye was taken with the help of UV-vis spectrophotometer. Molecular structure of Methylene blue dye is illustrated in Fig-2.1.This dye is a toxic chemical primarily used as a dye. It is a blue powder, and very soluble in water. The dye solution was prepared with the help of single distilled water.

Structure of dye:

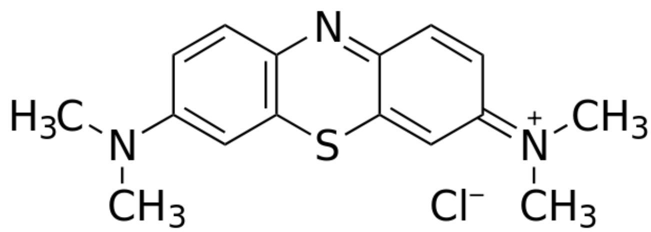


Fig2.1: Molecular structure of Methylene blue dye

2.4 Photoreactor at lab level during photocatalytic treatment

Fig: 2.2 Glass bowl reactor with magnetic stirrer on lab scale

Fig: 2.3 UV-vis Spectrophotometer

2.5 Method

2.5.1 Synthesizing ZnO/Ag under proper conditions

The effect of Ag dopant concentrations (5, 10, 25, 50 mmol) on the preparation of Ag doped ZnO synthesized via a sample precipitation method using zinc oxide and silver nitrate as precursors and sodium hydroxide as a precipitate agent.

2.5.1.1 Prepare 0.5 M ZnO solution for 100 ml

2.5.1.2 Prepare $AgNO_3$ for 50 mmol

2.5.1.3 Prepare NaOH solution for 50 ml by mixing 0.16 M NaOH with water

2.5.1.4 Mix 0.4 M glucose solution with the ZnO solution for 50 ml

2.5.1.5 Adjust the pH of the ZnO solution to pH 10 by dropping NaOH solution

2.5.1.6 Stir the solution by using magnetic stir for 1 hour at 300 rpm

2.5.1.7 Mix $AgNO_3$ with ZnO solution

2.5.1.8 Mix the glucose solution with ZnO solution stir for 2 hours at 300 rpm

2.5.1.9 Clean the solution with distilled water and methyl alcohol

2.5.1.10 Filtrate the solution and burn at 400° C for 5 hours

2.5.2 ZnO/Ag efficiency test with methylene blue

2.5.2.1 Mix ZnO/Ag powder with $1x10^{-5}$ M methylene blue

2.5.2.2 Stir the solution with magnetic stir in a dark room

2.5.2.3 Collect the sample every 30 minutes to find the adsorbent of stock

2.5.2.4 Turn on UV-light lamp and collect the sample every 30 minutes for 5 hours

2.5.2.5 Measure the adsorbance by UV-vis spectrometer

2.5.2.6 Repeat the method using fluorescent light instead

2.5.3 Forming ZnO/Ag on the rubber sheet

2.5.3.1 Prepare 8.4 %v/v rubber solution for 10 ml by mixing 60% rubber compound with distilled water

2.5.3.2 Mix ZnO/Ag with 10 %w/v ammonia solution for 10ml

2.5.3.3 Mix both solutions together and stir by magnetic stir for 15 minutes

2.5.3.4 Filtrate the solution by using vacuum filter

2.5.3.5 Heat the solution at 60°C for 3 hours

2.5.3.5 Air filtrate solution overnight at room temperature

2.5.3.6 Test the efficiency of ZnO/Ag formed on the rubber sheet and compare with the efficiency of the unformed ZnO/Ag and study the recyclable ability

2.5.4 Characteristics of ZnO/Ag powder

The prepared samples were characterized by X-ray powder diffraction (XRD), and scanning electron microscopy (SEM).

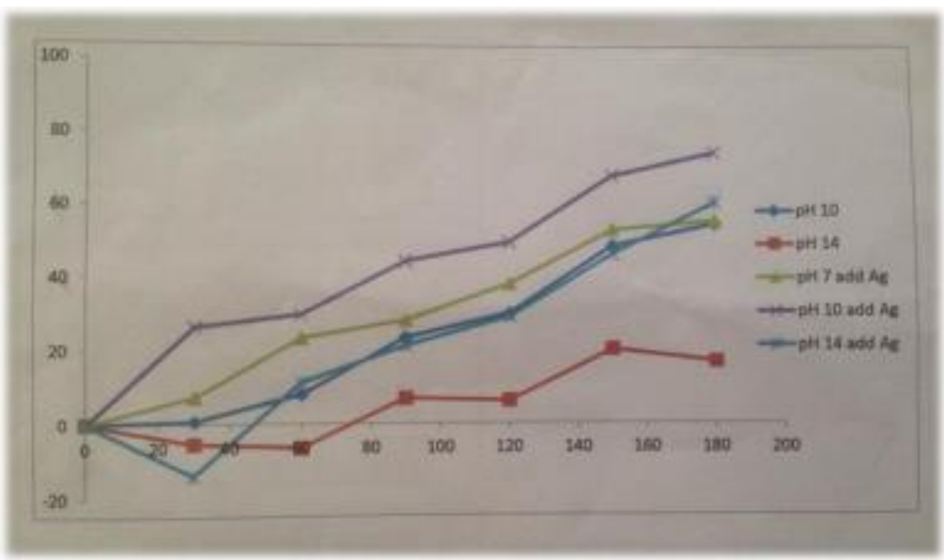
Chapter 3
Results

The photocatalytic treatment using ZnO/Ag catalyst was employed for the effective degradation of dye solution and textile mill wastewater in batch photo reactor at 298 K. A matrix of experimental variables was developed with varied ZnO/Ag dosage and pH**.**

3.1 Find the most proper pH condition for ZnO/Ag synthesis

The influence of the initial pH of the dye solution was studied as pH is considered to be one of the most important parameters that can affect the photo catalytic oxidation process. The initial pH of dye solution were varied from pH 7-14. The studies were carried out with 1.0×10^{-5} M Methylene blue dye solution and doses of catalyst**.**

%



time

Fig 3.1: The results from varied pH conditions

Obviously, it can be seen that the best pH condition for ZnO/Ag synthesis was at pH 10

3.2 Find the most proper ratio of Ag for ZnO/Ag synthesis

After optimizing pH, the catalytic dose is another important parameter which has a strong influence on the degradation kinetics of dye solution. ZnO/Ag catalyst was used in slurry mode. In order to determine the optimal amount of catalytic concentration, a series of experiments were carried out using different concentrations of ZnO/Ag catalyst varying from 5 to 50 mmol, at optimized pH of 10.0 with 1.0×10^{-5} M Methylene blue dye solution. The results are presented in Fig 3.2.

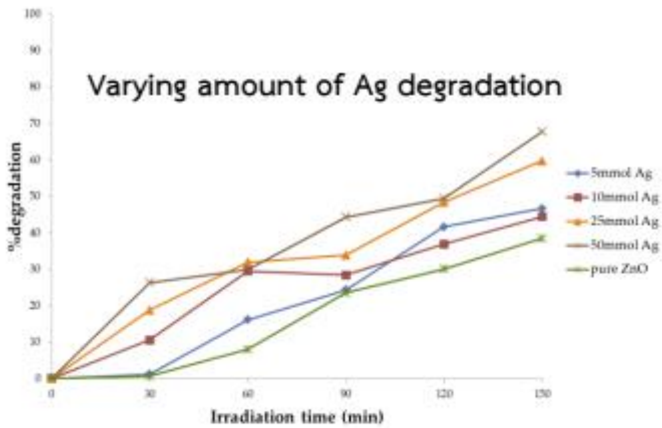


Figure 3.2: The results from varied Ag and ZnO ratio conditions

Obviously, it can be seen that the best Ag and ZnO for ZnO/Ag synthesis was at 50 mmol of Ag per 50 mmol of ZnO (1:1)

The results indicated that the best condition of ZnO/Ag to degrade methylene blue is when doped with 50 mmol of Ag at pH 10.

Mechanism of methylene blue degradation was obtained as seen in Fig 3.3

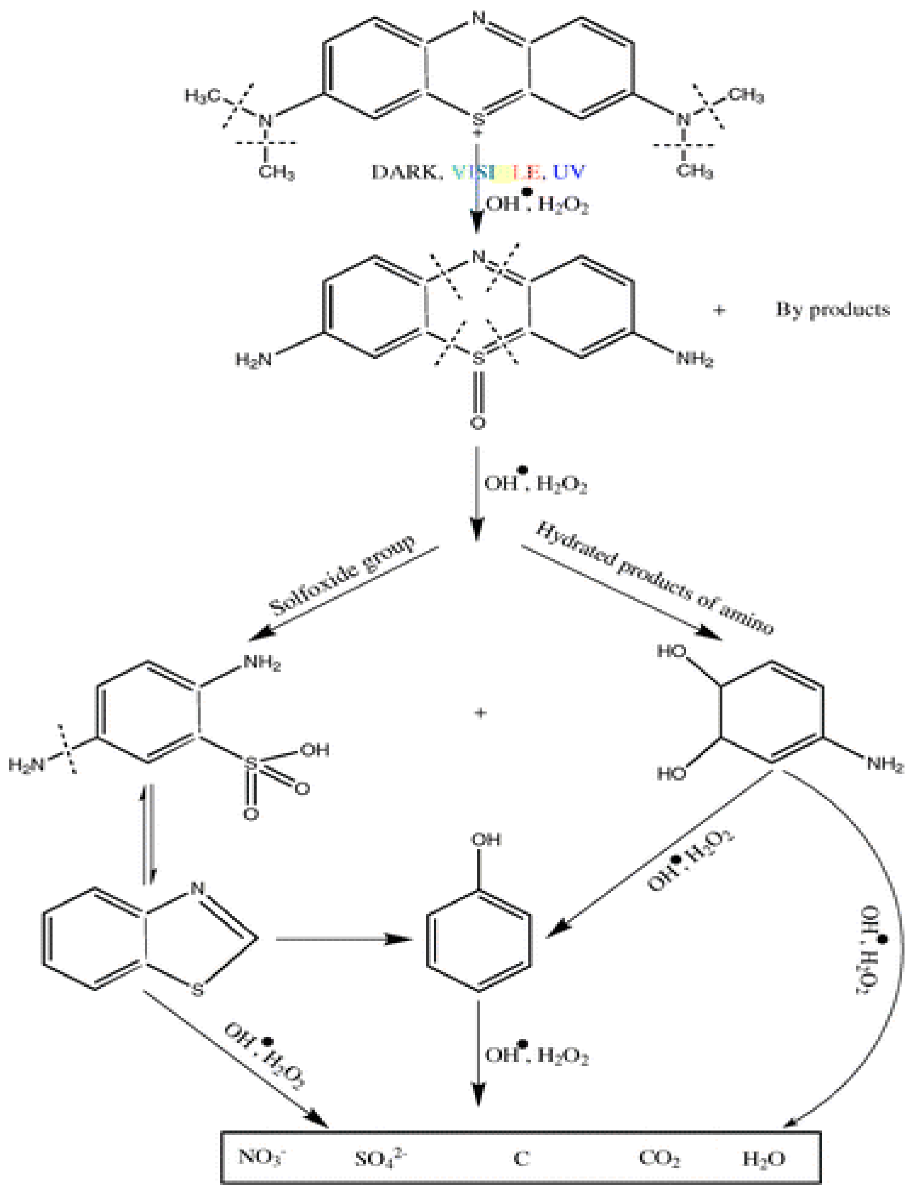
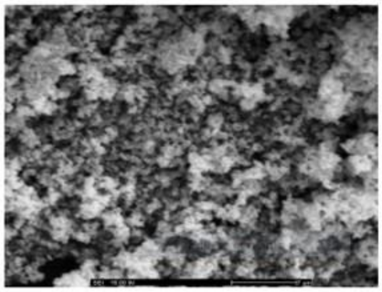


Fig 3.3 Mechanism of methylene blue degradation

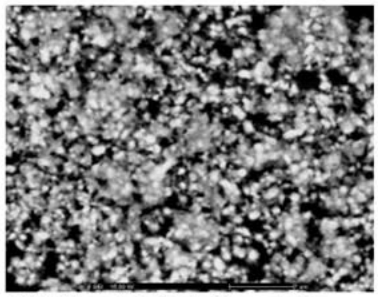
3.3 Results of characteristics of ZnO/Ag powder

The prepared samples were characterized using scanning electron microscopy (SEM) and X-ray powder diffraction (XRD).

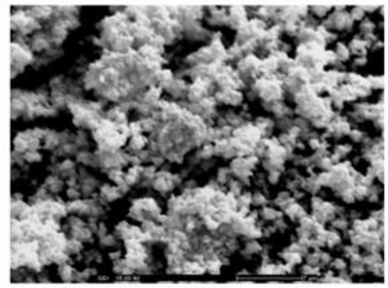
3.3.1 Scanning electron microscopy (SEM).



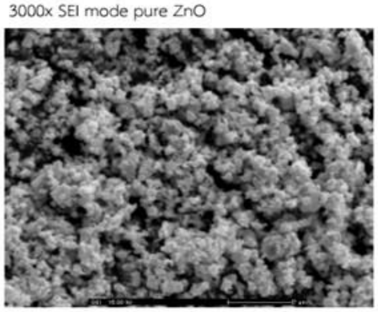
3000x SEI mode pure ZnO



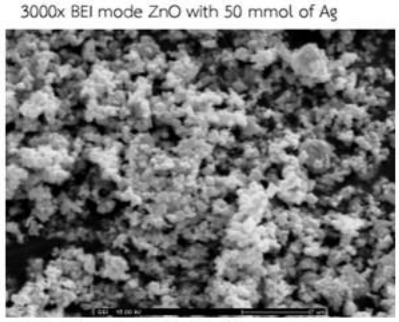
3000x BEI mode ZnO with 50 mmol of Ag



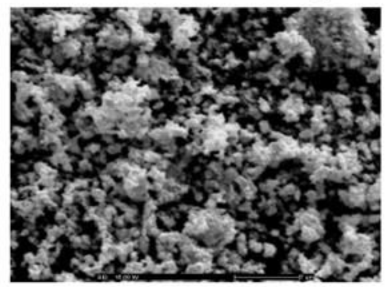
3000x SEI mode ZnO with 25 mmol of Ag



3000x SEI mode ZnO with 5 mmol of Ag

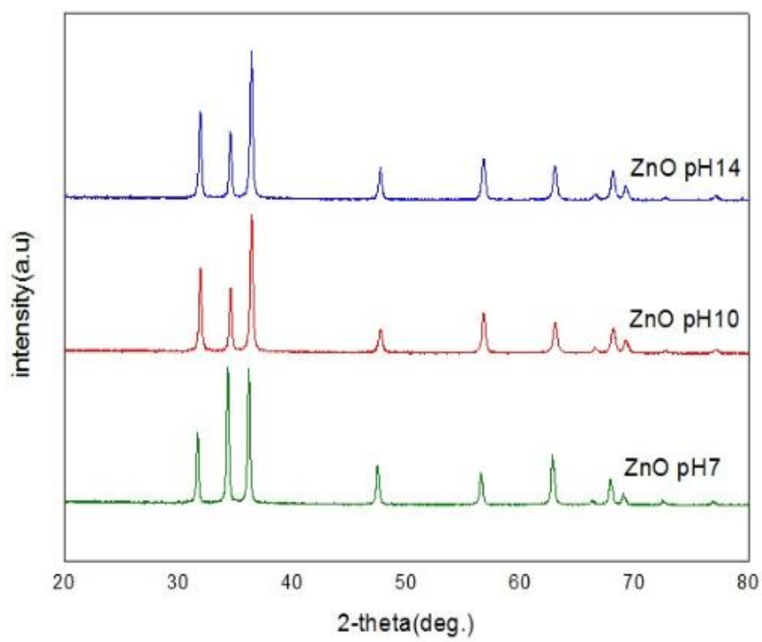


3000x SEI mode ZnO with 10 mmol of Ag



3000x SEI mode ZnO with 50 mmol of Ag

3.3.2 X-ray powder diffraction (XRD).



3.4 The efficiency test of ZnO/Ag-strewn rubber sheet

Figure 3.4: ZnO-strewn rubber sheet

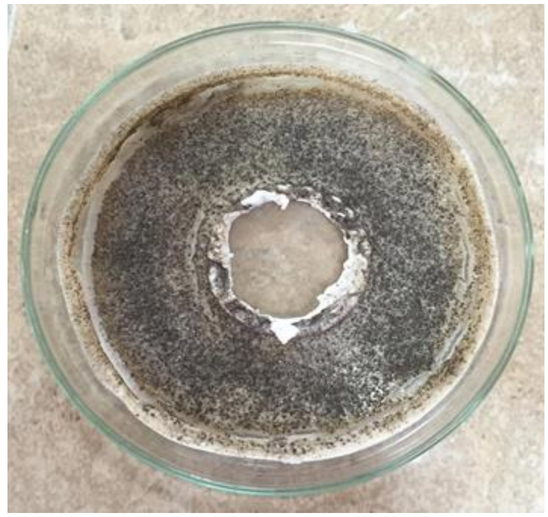


Figure 3.5: ZnO/Ag-strewn rubber sheet

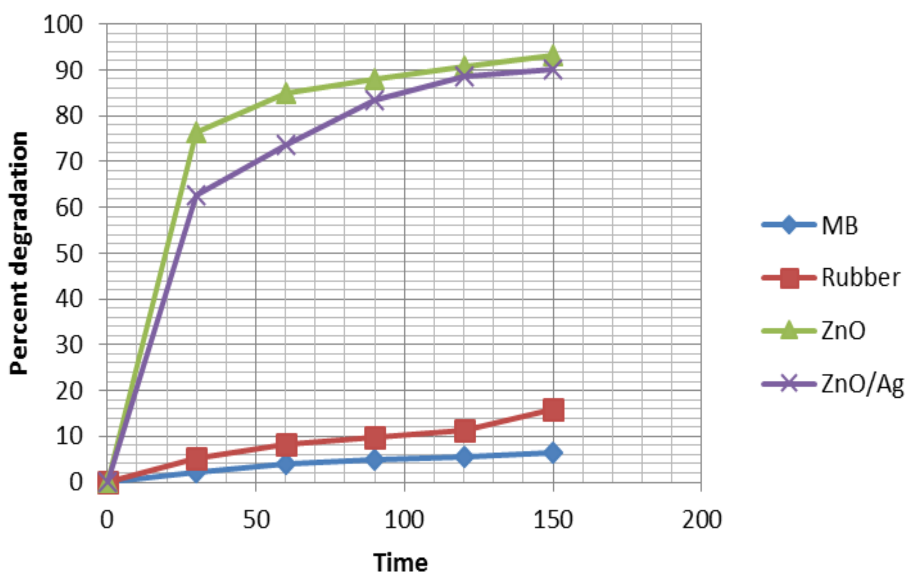


Figure 3.6: The test of Methylene Blue degradation under UV light

From the results, the trend of degradation of methylene blue in ZnO and ZnO/Ag -were the same. So, there were no differences between ZnO/Ag-strewn rubber sheet and ZnO-strewn rubber sheet

3.5 The efficiency test of ZnO/Ag in rubber composites

Figure 3.7: 2.5% ZnO-rubber composites

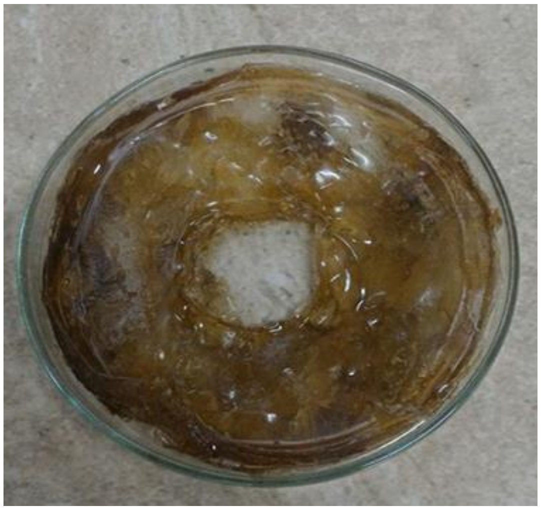


Figure 3.8: 2.5% ZnO/Ag-rubber composites

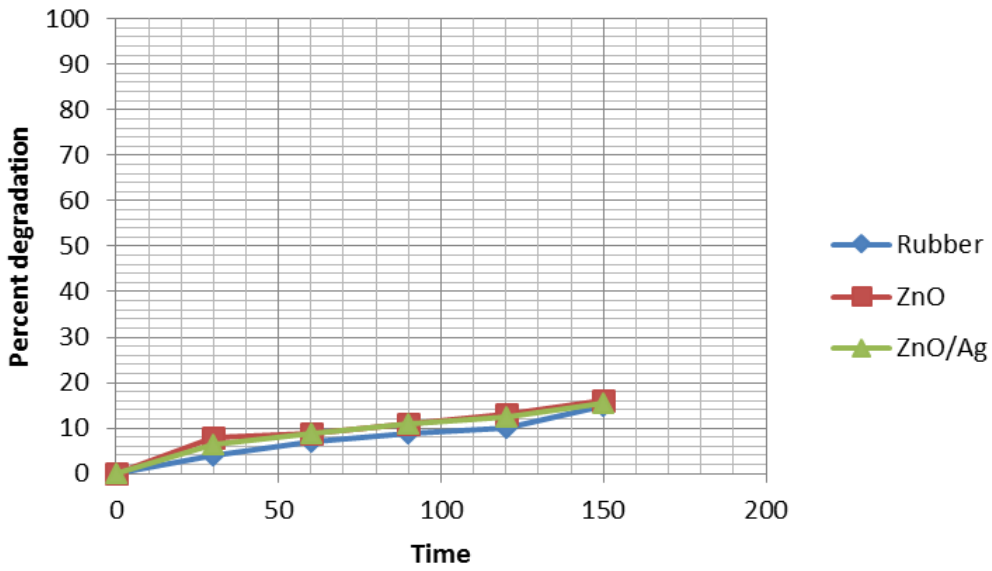


Figure 3.9: The test of Methylene Blue degradation under UV light

From the results, the degradation trends of methylene blue in ZnO and ZnO/Ag were the same. So, there were no difference between ZnO/Ag and ZnO in rubber composites. And from the graph, it showed that the percentage degradation of methylene blue changed a little which may be caused by surface absorption, and not from photocatalytic reaction.

Chapter 4

Conclusion

This project studied the photocatalytic activity of ZnO under various conditions. We can conclude that pH = 10 and Ag 50 mmol provided the best condition that made ZnO most efficient to be a catalyst. If we look at SEM and XRD results, we can observe that pH and Ag affected shape, the capture of ZnO crystal and rate of reaction because when the electrons at valence band received energy from light, they moved up to conduction band. But the electrons could move down to valence band combined with electron hole (h+) again. We call this phenomenon “recombination”, But Ag at the surface of ZnO received electrons from conduction band of ZnO, resulting in the decrease in recombination and increase in the rate of reaction.

After we synthesized ZnO/Ag, we tested with methylene blue and formed on rubber composites. The results showed that rubber strew sheet ZnO and ZnO/Ag can degrade the nearby methylene blue because the substance was ZnO, while changing pH and add Ag could not reduce Bandgap energy. Moreover, ZnO on rubber compound could not degrade methylene blue because ZnO/Ag was coated by rubber sheet.

References

J.Zhang, L.j.Xu, Z.Q.Zhu, Q.J.Liu. (2015). Synthesis and properties of (Yb,N)-TiO_2 photocatalyst for degradation of methylene blue under visible light irradiation. Materials Research Bulletin.

Shila Jafari, Feiping Zhao, Dongbo Zhao, Manu Lahtinen, Amit Bhatnagar, Mika Sillanpaa. (2015). A comparative study for the removal of methylene blue dye by N and S modified TiO_2 Absorbents. Journal of Molecular Liquids.

R.Barreiro-Iglesias, R.coronilla, A.Concheiro, C.Alvarez-Lorenzo. (2015). Preparation of chitosan beads by Simultaneous cross-linking/insolubilisation in basic pH Rheological optimization and drug loading/release behavior. EuropeanJournal of Pharmaceutical Sciences

S.M.Hosseini, I.Abdolhosseini Sarsari, P.Kameli, H.Salamati. (2015). Effect of Ag doping on structural, optical, and photocatalytic properties of ZnO nanoparticles. Journal of Alloys and Compounds

Mu-Hsiang Hsu, Chi-Jung Chang. (2015). Ag-doped ZnO nanorods coated metal wire meshes as Hierarchical photocatalysts with high visible-light driven photoactivity and photostabillity. Journal of Hazardous Materials

Jun Wang , W., Zhaohong Zhang , Z., Rui Xu , Y., and Xiangdong Z. (2007) "Treatment of nano-sized rutile phase TiO_2 powder under ultrasonic irradiation in hydrogen peroxide solution and investigation of its sonocatalytic activity", ultrasonic sonochemistry