Zn/ZnO/TiO$_2$ and Al/Al$_2$O$_3$/TiO$_2$ Photocatalysts
for the Degradation of Cypermethrin

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Abstract

The aim of the present study is to investigate the activity of semiconductor materials on the degradation of pesticides cypermethrin under UV-light (6 W, λ = 354 nm). Three types of photocatalysts were prepared namely Zn/ZnO, Zn/ZnO/TiO$_2$ and Al/Al$_2$O$_3$/TiO$_2$. Zn/ZnO film was prepared by anodic oxidation of zinc in NaOH with various concentrations (0.2, 0.3, 0.4, and 0.5 M) at 12 V for 20 minutes. The best concentration for NaOH is 0.5 M and the best applied voltage in the preparation of Zn/ZnO is 12 V. The Al/Al$_2$O$_3$ film was prepared by anodizing aluminium plate in H$_2$SO$_4$ at 12 V for 60 minutes. TiO$_2$ films were electrodeposited onto Zn/ZnO and Al/Al$_2$O$_3$ by electrolysis technique in (NH$_4$)$_2$[TiO(C$_2$O$_4$)] solution at 12 V for 20 minutes. Zn/ZnO/TiO$_2$/UV shows the highest photocatalytic degradation of cypermethrin compared to the other photocatalytic system. The effects of some operational parameters such as pH and oxidizing agent (H$_2$O$_2$) on the degradation efficiency of the semiconductor were also studied. The optimum pH for the photodegradation of cypermethrin using Zn/ZnO is pH 5. In the presence of H$_2$O$_2$ as the oxidizing agent, the overall reaction is significantly reduced due the scavenging effect of H$_2$O$_2$. The surface morphology of the catalyst was studied by FESEM analysis.

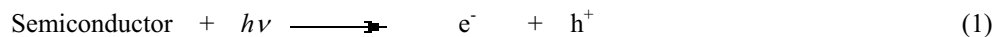**Keywords:** Zinc oxide, Titanium dioxide, Anodic oxidation, Photodegradation, Cypermethrin

1. Introduction

The used of chemical in agricultural activity to increase the production is a common phenomenon. This activity, however, will generate residues that can be noxious to the environment. Cypermentrine is a common active chemical in household and outdoor insecticides, also used as pesticides for the bovine ticks control. The used of cypermentrine will produce hundreds of liters of residual solution, which could be indiscriminately discarded the water system and should be treated.

Photocatalytic degradation has been proven to be a promising method treating water contaminated with organic and inorganic pollutants, including pesticides [Devipriya and Yeshodharan, 2005]. The term photocatalysis is defined as a catalytic reaction involving light adsorption by a catalyst or a substrate.

TiO$_2$ is a promising material as a photocatalyst for the photodecomposition reactions and is widely used for water treatment processes. Recently, various preparation and fixation methods for TiO$_2$ had been reported   [Ishikawa and Matsumoto, 2002]. Several practical problems arising from the use of TiO$_2$ powder are obvious during or after photocatalytic processes. Thus, an alternative form of TiO$_2$ has been reported. TiO$_2$ thin film has been successfully used for the photocatalytic degradation of organic compounds [Andronic and Duta, 2007]. There are several of preparation methods to obtain TiO$_2$ thin films, including spray coating, spin coating, chemical vapour deposition, sol-gel and electrodeposition method. Electrodeposition is a low-cost electrochemical method in which TiO$_2$ photocatalyst is directly deposited on the metal oxide substrate [Ishikawa and Matsumoto, 2001].

Although TiO_2 is the most commonly used photocatalyst, ZnO is found to be a suitable alternative to TiO_2 since ZnO has the same band gap energy and similar photodegradation mechanism   as TiO_2 (Equation 1 – 5) [Yamaguchi et al., 1997]. TiO_2 anatase band gap energy is 3.2 eV while ZnO band gap energy is 3.17 eV. Superoxide anion radicals (•O_2^-) and hydroxyl radicals (•OH) generated (Equation 2-3) in the aqueous medium are responsible in accelerating the oxidation of pollutants [Mills and Hunte, 1997 and Vidal et al., 1999].

$$Semiconductor \ + \ h\nu \ \longrightarrow \ e^- \ + \ h^+ \tag{1}$$

$$O_2 \ + \ e^- \ \longrightarrow \ •O_2^- \tag{2}$$

$$H_2O + \ h^+ \ \longrightarrow \ •OH + H^+ \tag{3}$$

$$OH^- \ + \ h^+ \longrightarrow \ •OH \tag{4}$$

$$•OH + H^+ \ \longrightarrow \ •OH_2 \tag{5}$$

Under certain conditions, ZnO has been reported to be more effective than TiO_2. However, the photocorrosion of ZnO which frequently occurs when the photocatalyst is illuminated under UV-lights decreases its photocatalytic activity in the aqueous solutions [Yamaguchi et al., 1997].

The photocatalytic efficiency of the photocatalysts can be enhanced by coupling the ZnO with TiO_2 [Yang and Swisher, 1996].   The coupling of two semiconductors provides a novel approach to the enhancement of photocatalytic activity. Recent, studies had shown that binary oxides can provide a more efficient charge separation, increased lifetime of charge carriers and enhanced interfacial charge transfer to absorbed substrates [Wang et al., 2002]. Studies had been conducted on the photocatalytic activity using the binary semiconductor oxide system such as TiO_2/SnO_2, TiO_2/ZrO_2, TiO_2/MoO_3, TiO_2/CdS, TiO_2/Fe_2O_3, TiO_2/WO_3, CdS/ZnO, CdS/AgI, and ZnO/ZnS [Wang et al., 2002, Liao et al., 2004 and Liao et al., 2008].

Liao *et al.* (2004) studied the preparation and photocatalytic activity of the binary oxide photocatalyst ZnO/TiO_2 in the degradation of methyl orange dye. It was shown that the addition of ZnO enhanced the photocatalytic activity of TiO_2 significantly.

This paper covers the degradation reaction of cypermethrin using electrodeposition coated TiO_2 photocatalysts. The photocatalysts were characterized using X-Ray Diffraction (XRD) and Field Emission Scanning Electron Microscopy (FESEM) technique. The photodegradation of cypermethrin was conducted in the presence of UV-light and monitored by UV-Visible spectroscopy. Degradation process is the process of breaking organic molecules into smaller molecules which will further mineralize into minerals such as NO_3^-, PO_4^{3-}, CO_3^{2-}, depending on the elements present in the molecule.

2. Experimental

2.1 Anodic deposition of ZnO thin film on zinc sheet.

The ZnO thin film was prepared by modification of Yamaguchi's method [Yamaguchi et al.,1997]. A zinc sheet (50 x 60 x 0.38 mm) was used as the substrate for anodizing. The surface was scrubbed by sandpaper and etched by immersing in 0.1 M NaOH for 3 minutes and followed by washing in distilled water. The zinc plate was set as the anode while a graphite plate was set as the cathode and both plates were placed at a distance of 50 mm for one another in NaOH aqueous solution (0.2, 0.3, 0.4, 0.5 M). A DC voltage (12 V) was applied for 20 minutes using a constant voltage power supply of PL Regulated 303 DC. The plate obtained was referred as Zn/ZnO. The plate prepared using 0.2, 0.3, 0.4 and 0.5 M NaOH was denoted as Z02, Z03, Z04 and Z05 respectively.

A similar procedure was repeated using aluminium plate and replacing the NaOH with 3.0 M H_2SO_4. The alumite plate obtained was referred as Al/Al_2O_3.

2.2 The preparation of TiO_2 thin film on zinc oxide substrate by electrodeposition process.

TiO_2 was electrodeposited into the pores of Zn/ZnO (Zn/ZnO/TiO_2) by alternative electrolysis in a mixed aqueous solution containing $(NH_4)_2[TiO(C_2O_4)_4]$ (1×10^{-2} M) and $(COOH)_2$ (2.5×10^{-3} M) which was adjusted to pH 4 by titration with NH_4OH, under a DC voltage (12 V) for 20 minutes. The distance between the cathode (Zn/ZnO) and anode (graphite) was fixed at 50 mm. The plate obtained was referred as Zn/ZnO/TiO_2 (Z05T). The process adjusted was a modification of Ishikawa's method [Ishikawa and Matsumoto, 2001 and Ishikawa and Matsumoto, 2002].

A similar procedure was repeated using alumite plate, Al/Al_2O_3.   The plate obtained was referred as $Al/Al_2O_3 /TiO_2$ (A3T).

2.3 Photodegradation of cypermethrin using prepared photocatalysts.

The photocatalytic activity of the prepared Zn/ZnO, Zn/ZnO/TiO_2 and $Al/Al_2O_3/TiO_2$ catalysts were determined by the photodegradation of cypermethrin.

Cypermethrin with a concentration of 1.0×10^{-3} M (5 mL) was pipetted into a square pyrex reactor and 45 mL of distilled water was added to dilute the sample solution to 1.0×10^{-4} M. The solution was then stirred with magnetic stirrer for 10 minutes. The Zn/ZnO plate was then dipped into the sample. An Ultra Violet lamp (6 W, 354 nm) was used as the light source in this experiment.

For the first 90 minutes, the sample was allowed to be adsorbing on the surface of the catalyst support. Within this period, 3 mL of the sample was taken out using syringe at 0, 30, 60 and 90 minutes. Then, the sample was irradiated with UV lamp for the next 3 hours. Sample was taken out at 30, 60, 90, 120, 150 and 180 minutes and analyzed using Shimadzu 2510PC UV/Visible spectrophotometer. The percentage of degradation was calculated using Equation 6.

$$\% \text{ Degradation} = (A_o - A_t)/A_t \times 100 \qquad (6)$$

where,

A_o = initial absorption

A_t = absorption at time, t.

3. Results and Discussion

3.1 Optimization of the NaOH Concentration for the Preparation of Zn/ZnO

The optimum NaOH concentration was determined from the photocatalytic activity of the prepared catalysts. A plot of the percentage degradation as a function of time is shown in Figure 1. The percentage degradation of cypermethrin is seen to increase upon irradiation of UV-light. Zn/ZnO prepared with the highest concentration of NaOH (Z05) gives 67.5% degradation indicating the highest percentage of cypermethrin degradation as shown in Figure 1. Thus, 0.5 M NaOH is considered the most suitable concentration in the preparation of Zn/ZnO photocatalyst.

3.2 Photolysis and Photocatalytic Degradation of Cypermethrin

The degradation of cypermethrin by photolysis and photocatalysis is shown in Figure 2. Cypermethrin in the aqueous solution was treated under UV-light alone and in the presence of Zn/ZnO as the photocatalyst. Photodegradation in the absence of Zn/ZnO gives lower degradation of cypermethrin (47.4%) within 270 min. In contrast, 67.5% cypermethrin is photodegraded within 270 min in the presence of Zn/ZnO. These experimental results demonstrate that the direct photolysis has improved by the presence of heterogeneous photocatalyst. The photocatalyzed degradation of organic matter in aqueous solution is initiated by the photoexcitation of the semiconductor, followed by the formation of high energy states of electron-hole pair on the surface of the catalyst which can further provide a powerful oxidative species such as the hydroxyl radical.   This strong oxidizing ●OH radical can promote the mineralization of organic matter [Daneshvar et al., 2007].

3.3 The Effect of Initial pH value

Figure 3 shows the effect of initial pH value on the photocatalytic degradation of cypermethrin in the presence of Z05. In neutral or acidic aqueous solution, cypermethrin hydrolyzes slowly, with hydrolysis being more rapid at pH 9 [International Programme on Chemical Safety,1989]. However, the results show that the percentage of cypermethrin degradation at pH 2 (49.3%), due to photocorrosion is higher than pH 12 (23.9%). Cypermethrin is photodegraded the most at pH 5 (69.1%) which is the original initial pH of the sample solution.   At a pH lower than 4, ZnO undergoes photocorrosion through self-oxidation and tends to dissolve in the acidic solution. Moreover, upon irradiation under UV light, there is a higher possibility for the formation of photocatalytically inert $Zn(OH)_2$ compound on the surface layers of the catalyst that will cause surface passivation which will deactivate the photocatalytic activity.

3.4 The Effect of Hydrogen Peroxide

The effect of H_2O_2 had been investigated in numerous studies and is observed to increase in the photodegradation rate of organic hazard pollutants. Even though H_2O_2 is a strong oxidant, it decreases the photodegradation rate of cypermethrin as shown in Figure 4. This is probably due to the scavenging effect of H_2O_2 which can reduced the production of •OH in the solution [Daneshvar et al., 2007]. It is proven that the presence of hydroxyl radical exceeding the optimum amount could lead to the recombination of the radicals forming water [International Programme on Chemical Safety,1989].

3.5 The Photocatalytic Activity of Zn/ZnO, Zn/ZnO/TiO$_2$ and Al/Al$_2$O$_3$/TiO$_2$

A comparative study was conducted to investigate the photocatalytic activity of Zn/ZnO (Z05), Zn/ZnO/TiO$_2$ (Z05T) and Al/Al$_2$O$_3$/TiO$_2$ (A3T) in the degradation of cypermethrin. The results are shown in Figure 5. Z05T gives the highest percentage of degradation compared to Z05 and A3T where 75.3% of cypermethrin is degraded under irradiation of UV-light. The binary catalyst, Zn/ZnO/TiO$_2$ has performed better on degrading cypermenthrin compared to single catalyst Zn/ZnO. According to the experimental results, it can be demonstrated that the binary oxide provides more active sites and thus enhances the photocatalytic activity, compared to ordinary oxide.

The photocatalytic activity can be explained through inter-particle electron transfer pathway (IPET) of the binary semiconductor [Serpone et al., 1995]. The higher photocatalytic activity of $Zn/ZnO/TiO_2$ can be related to the roles of electrons and holes of the catalyst which can possess different redox energy levels for their corresponding conduction and valence bands [Serpone et al., 1995 and Michaelis et al., 2006]. In $Zn/ZnO/TiO_2$, the electron transfer occurs from the conduction band of the photo-activated ZnO to the conduction band of photoactivated TiO_2 and conversely. The holes move in the opposite direction from the electron. This vectorial displacement of electrons and holes provides a more efficient charge separation and increases the charge carrier's lifetime. Thus the recombination of electron and holes in this catalyst can be greatly suppress and the efficiency of the interfacial charge transfer between the adsorbed substrate and catalyst can be enhanced [Liao et al., 2008 and Zhang et al., 2004].

A3T is even less effective on the photocatalytic of cypermenthrin which give only 60.4% degradation in the UV-induced degradation process compared to the other two catalysts. The experimental results indicate that TiO_2 works more effectively in the UV-induced degradation of these pesticides.

Aal *et al.* (2008) demonstrated that the noble binary oxide, TiO_2/ZnO is more effective in promoting the degradation of 2-chlorophenol compared to pure ZnO. Moreover, the addition of ZnO as a substrate could enhance the activity of TiO_2 significantly [Liao et al., 2004]. Chu (2007) had investigated on the photodegradation of 4-nitrophenol and chlordance using Zn/ZnO and $Zn/ZnO/TiO_2$ photocatalysts and reported that binary metal oxide is more efficient.

3.6 Characterization of Photocatalyst

Figure 6 illustrates the FESEM images for Z04, Z05 and Z05T. The surface morphology of Z04 film shows a clear roughness associated to the presence of cavities and protuberances. In contrast, a clear open porous structure is observed in Z05 film, thus exhibits a much larger specific surface area than Z04 film. Therefore, the highest result in UV-induced degradation of cypermethrin of Z05 can be explained by this observation. The morphological properties of anodic ZnO layer can be correlated with the concentration of NaOH electrolyte solution in the electrodeposition process. As can be seen from Figure 6 (c), Z05T give a much higher open porous structure compared to Z05 photocatalyst. The increased in porosity will increase the specific surface area.

3.7 Elemental Analysis: Electron Dispersive X-Ray Analysis (EDX)

Figure 7 shows the EDX spectrum of Z05 photocatalyst. From the spectrum, it is observed that only two elements, Zn and O are present in the Z05 film. All elements present in the Z05 film are tabulated in Table 1.

The composition of element present in $Zn/ZnO/TiO_2$ (denoted as Z05T) is also detected using EDX analysis. The EDX spectrum of Z05T is illustrated in Figure 8. As can be seen from the EDX spectrum, an additional element is present in the Z05T which is titanium (Ti) element. The composition percentage for all elements present in Z05T is tabulated in Table 2. The existence of carbon may possibly come from graphite which is used as the cathode in the catalyst preparation.

4. Conclusion

Zn/ZnO, $Zn/ZnO/TiO_2$ and $Al/Al_2O_3/TiO_2$ photocatalyst systems were successfully synthesized in this study. Zn/ZnO cannot be used either in the acidic or in the basic conditions. Higher efficiency of photocatalytic degradation of cypermethrin is achieved at pH 5. The presence of high concentration of H_2O_2 which act as scavenger consequently reduced the efficiency of the photocatalyts. $Zn/ZnO/TiO_2/UV$ shows the highest photocatalytic efficiency compared to other system in the degradation of cypermethrin.

References

Aal, A. A., Barakat, M.A. and Mohamed, R.M. (2008). Electrophoreted Zn–TiO_2–ZnO nanocomposite coating films for photocatalytic degradation of 2-chlorophenol. *Appl. Surf. Sci*. Article in press.

Andronic, L. and Duta, A. (2007). TiO_2 Thin Films for Dyes Photodegradation.*Thin Solid Films*. 515: 6294–6297.

Chu, C. L. (2007). The preparation of titanium dioxide deposited onto alumite and zinc oxide catalysts for chlordance and 4-nitrophenol photodegradation. Universiti Teknologi Malaysia. B. Sc. Thesis.

Daneshvar, N., Aber, S., Seyed, M.S., Dorraji, Khataee, A.R., and Rasoulifard, M.H. (2007). Photocatalytic Degradation of the Insecticide Diazinon In The Presence of Prepared Nanocrystalline ZnO Powders Under Irradiation of UV-C Light. *Sep. Pur. Technol*. 58: 91-98.

Devipriya, S. and Yeshodharan, S. (2005). Photocatalytic Degradation of Pesticide Contaminants in Water. *Sol. Energy Mater. Sol. Cells*. 86: 309-348.

International Programme on Chemical Safety. (1989). *Environmental Health Criteria 82: Cypermethrin*. Geneva: World Health Organization.

Ishikawa, Y. and Matsumoto, Y. (2001). Electrodeposition of TiO_2 photocatalyst into nano-pores of hard alumite. *Electrochim. Acta.* 46: 2819–2824.

Ishikawa, Y. and Matsumoto, Y. (2002). Electrodeposition of TiO_2 photocatalyst into porous alumite prepared in phosphoric acid. *Solid State Ionics* .151: 213– 218.

Liao, D.L., Badour, C.A. and Liao, B.Q. (2008). Preparation of nanosized TiO_2/ZnO composite catalyst and its photocatalytic activity for degradation of methyl orange. *J. Photochem. Photobiol., A: Chem.* 194: 11–19.

Liao, S., Huang, D., Yu, D., Su, Y. and Yuan, G. (2004). Preparation and Characterization of ZnO/TiO_2, $SO_4^{2-}/ZnO/TiO_2$ photocatalyst and Their Photocatalysis. *J. Photochem Photobiol., A: Chem.* 168: 7-13.

Michaelis E., Wohrle, D., Rathousky, J. and Wark, M. (2006). Electrodeposition of porous zinc oxide electrodes in the presence of sodium laurylsulphate. *Thin solid films.* 497: 163-169.

Mills, A. and Le Hunte, S. (1997). "An overview of semiconductor photocatalysis" *J. of Photochem. and Photobiol. A: Chemistry*, 108. 1-35.

Serpone, N.P., Maruthamuthu, P., Pelizezetti, E. and Hidaka, H. (1995). Exploiting the interparticle electron transfer process in the Photocatalyzed oxidation of phenol. 2-chlorophenol and pentachlorophenol: Chemical evidence for electron and hole transfer   between coupled semiconductors. *J. Photochem. Photobiol., A: Chem.* 85: 247-255.

Vidal, A., Dinya, Z., Mogyorodi Jr., F. and Mogyorodi, F. (1999). "Photocatalytic of thiocarbamate herbicide active ingredients in water." *Applied Catalyst B: Environ..* 21. 259–267.

Wang, C., Zhao, J., Wang, X., Mai, B., Sheng G., Peng P. and Fu J. (2002). Preparation, characterization and photocatalytic activity of nano-sized ZnO/SnO_2 coupled photocatalysts. *Appl. Catal., B: Environ.* 39: 269–279.

Yamaguchi, Y., Yamazaki, M., Yoshihara, S. and Shirakashi, T. (1997). Photocatalytic ZnO Films Prepared by Anodizing. *J. Electroanal. Chem.* 442: 1-3

Yang, J. and Swisher, J.H. (1996). "The phase stabilization of $Zn_2Ti_3O_8$." *Material Characterization*. 37. 153-159.

Zhang M., An, TO., Hu, X., Wang, C., Sheng, G. and Fu, J. (2004). Preparation and photocatalytic properties of a nanometer $ZnO-SnO_2$ coupled Oxide. Appl. Catal., A: Gen. 260: 215-222.

Tables and Figures

Table 1. The weight percentage of elements analyzed by EDX for Z05 photocatalyst

Element	Weight (%)
O	20.87
Zn	79.13
Totals	**100.00**

Table 2. The weight percentage of elements analyzed by EDX for Z05T photocatalyst

Element	Weight (%)
C	2.99
O	34.68
Ti	15.75
Zn	46.58
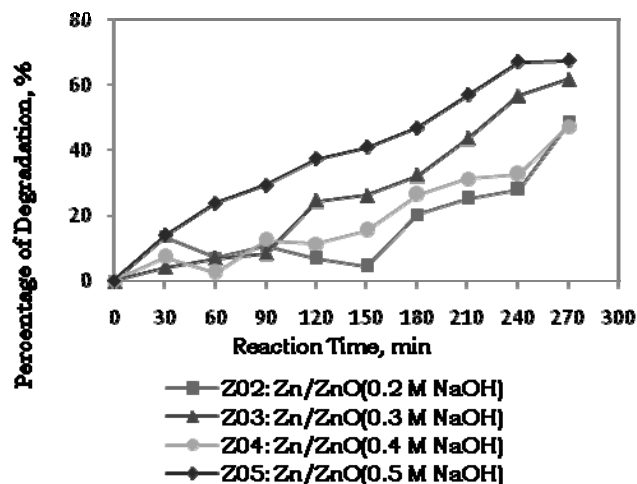
Figure 1. Percentage photodegradation of cypermethrin using Z02, Z03, Z04 and Z05 photocatalysts, UV (λ=254 nm), irradiated for 4 1/2 hours
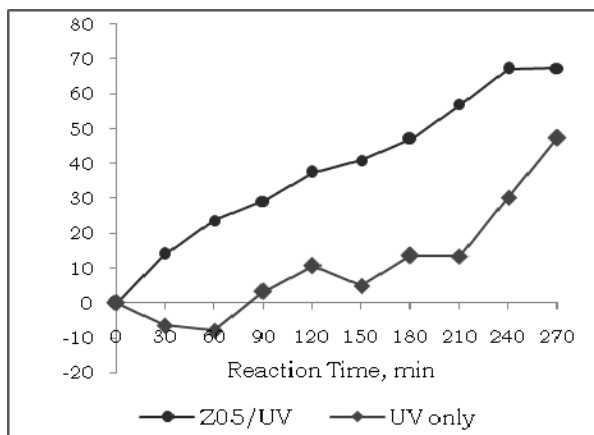
Figure 2. The degradation of cypermethrin by photolysis and photocatalysis under UV (λ=254 nm), irradiated for 4 1/2 hours.
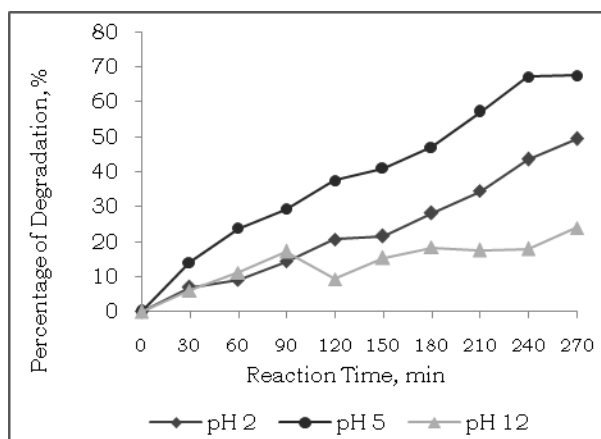
Figure 3. Effect of initial pH on the photocatalytic degradation of cypermethrin,
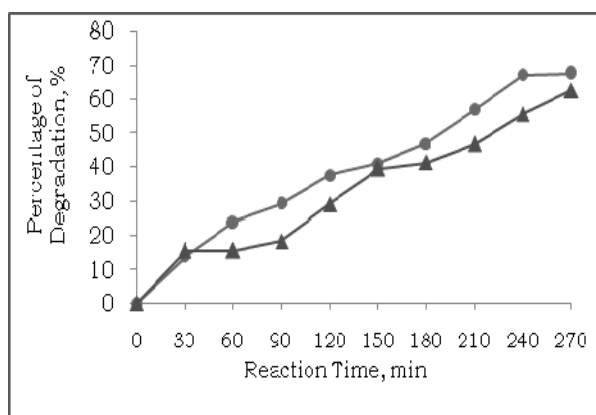using Z05 catalyst, UV (λ=254 nm), irradiated for 4 1/2 hours

Figure 4. The effect of hydrogen peroxide on the photocatalytic degradation of cypermethrin,
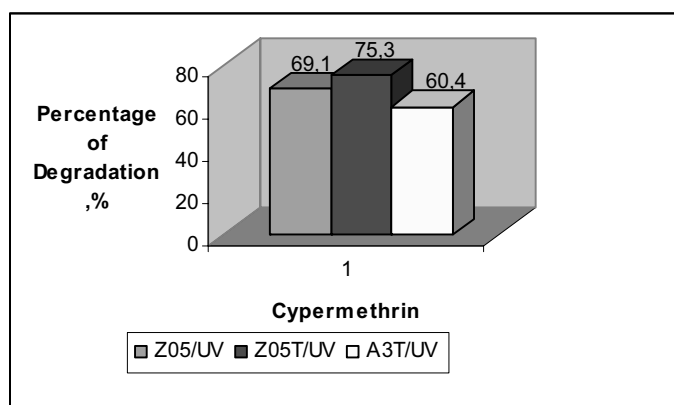using Z05 catalyst, UV (λ=254 nm), irradiated for 4 1/2 hours.

Figure 5. The percentage degradation of cypermethrin using Z05, Z05T and A3T catalysts,
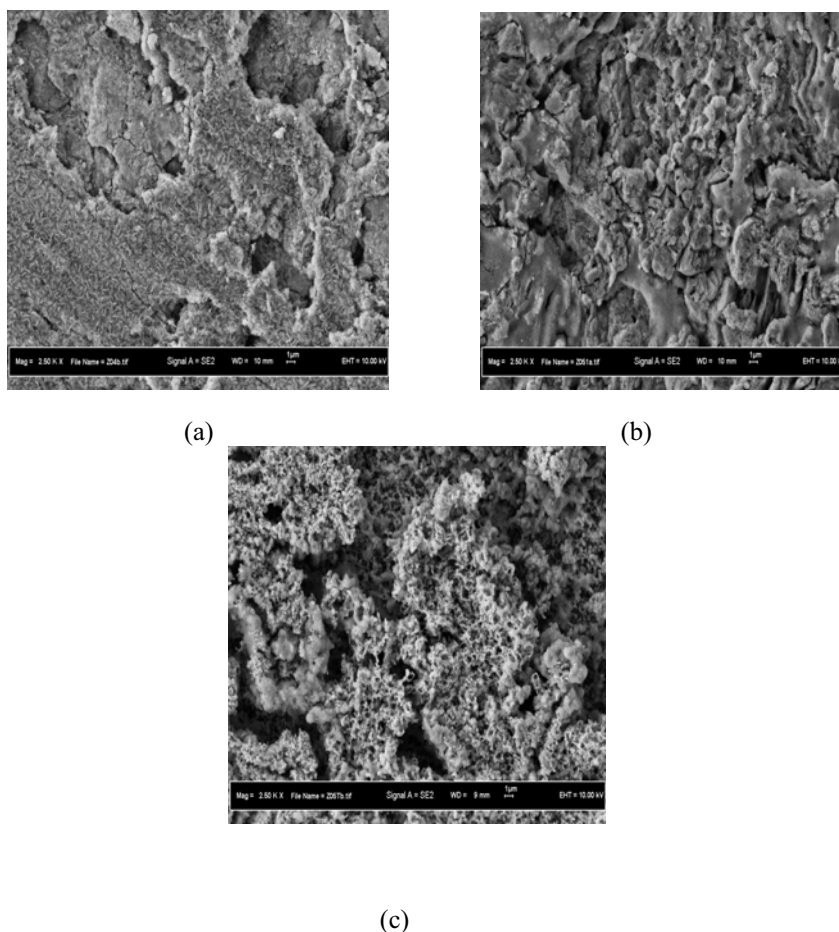UV (λ=254, nm), irradiated for 4 1/2 hour

(a)

(b)

(c)

Figure 6. The FESEM images of (a) Z04, (b) Z05, (c) Z05T at 2.5K magnification, 1 cm = 1 μm
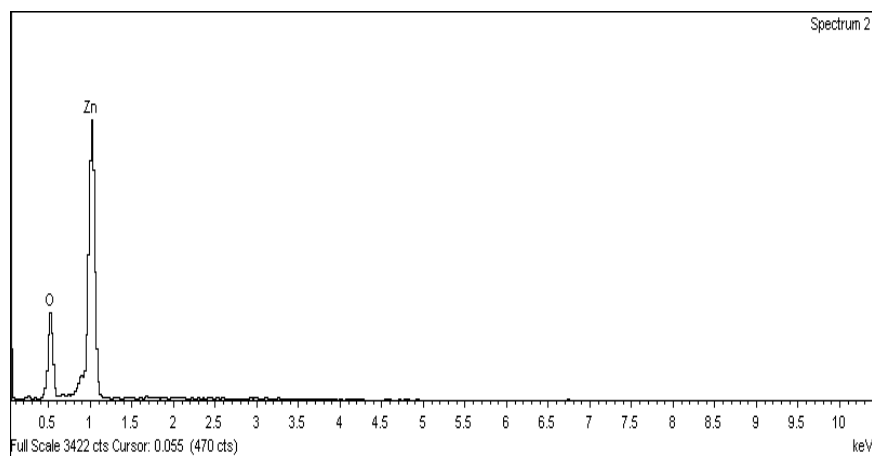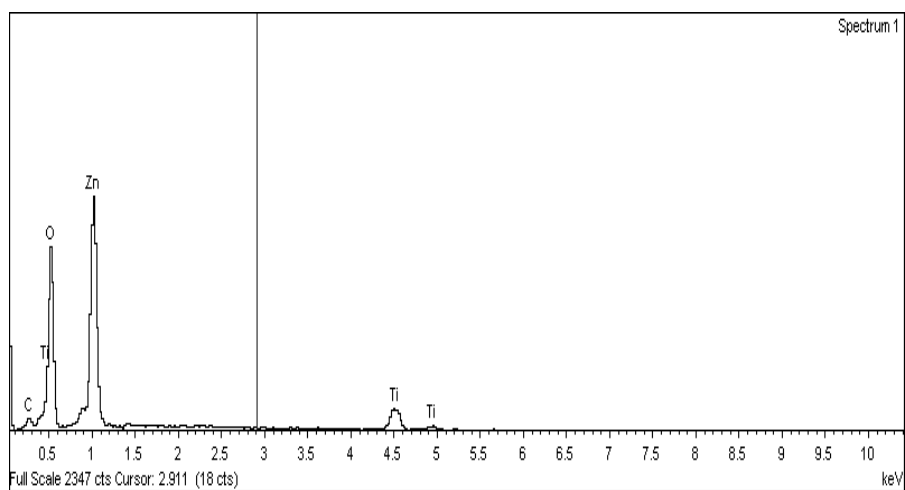

Figure 7. EDX spectrum of Z05 photocatalyst

Figure 8. EDX spectrum of Z05T photocatalyst