DEGRADATION STUDIES ON PARAQUAT AND MALATHION USING TiO_2/ZnO BASED PHOTOCATALYST

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Abstract

Paraquat, a herbicide and malathion, an insecticide are pesticides that are always polluting our water system. Thus a lot of efforts has been conducted to treat the polluted water. The latest technology proposed is using photocatalyst. In this study, ZnO and TiO_2 were used as photocatalysts to degrade the pesticide in the presence of UV light (λ=354 nm). The photodegradation rate was measured using UV-Visible spectrophotometer and TOC analyzer. Malathion showed the absorption peak at λ=210 nm while for paraquat at λ=258 nm. The best coupled photocatalyst for degrading malathion solution is ZnO/TiO_2 with % weight ratio 1:0.05 and the best coupled photocatalyst in degrading paraquat solution is TiO_2/ZnO with % weight ratio 1:0.03. The result shows that Fe^{2+} ion present in the reaction mixture was better than Fe^{3+} ion present as a dopant (which is added during the catalyst preparation). The optimum photocatalyst calcinations temperature for degrading paraquat and malathion were 550°C for TiO_2 and 500°C for ZnO. The physical properties of the best catalyst were characterized using SEM, XRD, UV-Vis-NIR spectrophotometer and elipsometer. By increasing the calcinations temperature up to 600°C, XRD data showed the transformation of TiO_2 anatase to rutile phase while for ZnO, the increment of the intensity of ZnO catalyst was observed, indicating that, the quality of ZnO wurtzite crystal was improved. The thicknesses for ZnO, ZnO/TiO_2 1:0.05 and ZnO/TiO_2 doping with Fe^{3+} thin film were 130.57 nm, 150.68 nm and 153.84 nm respectively. The band gap energy values measured using UV-Vis NIR were in the range of 2.95 – 3.09 eV.

Abstrak

Parakuat, sejenis racun rumpai dan malation sejenis racun serangga merupakan pesitisid yang mencemar sistem akuatik. Banyak usaha telah dijalankan masa kini untuk merawat air yang tercemar. Antara kaedah yang terbaru adalah teknik pemangkin foto. Dalam kajian ini, mangkinfoto TiO_2 dan ZnO telah digunakan untuk mendegradasikan larutan racun perosak dengan kehadiran sinaran ultralembayung (λ=354 nm). Kadar fotodegradasi diukur dengan menggunakan Spektrofotometer Ultralembayung-Nampak dan analisis TOC. Malation menunjukkan serapan pada λ=210 nm manakala parakuat pada λ=258 nm. Pasangan mangkin yang terbaik mendegradasi larutan malation adalah TiO_2/ZnO dengan nisbah % berat 1:0.05 manakala mangkin yang terbaik untuk mendegradasi larutan parakuat adalah pasangan mangkin TiO_2/ZnO dengan nisbah % berat 1:0.03. Kehadiran dopan yang ditambahkan dalam penyediaan mangkin, merencatkan tindak balas fotodegradasi manakala penambahan ion logam dalam larutan tindak balas meningkatkan peratus fotodegradasi. Mangkin TiO_2 yang dikalsin pada suhu 550°C dan mangkin ZnO yang dikalsinkan pada suhu 500°C memberikan peratus degradasi yang paling tinggi. Pencirian sifat fizik mangkin dikaji dengan menggunakan SEM, XRD, UV-Vis-NIR spektrofotometer dan elipsometer. Data XRD menunjukkan bahawa apabila suhu pengkalsinan dinaikkan ke 600°C, fasa anatas TiO_2 telah bertukar kepada fasa rutil. Sebaliknya untuk ZnO, peratus intensiti puncak ZnO didapati bertambah dengan pertambahan suhu pengkalsinan. Ini menunjukkan bahawa kualiti kristal wurzit ZnO bertambah baik. Ketebalan saput tipis bagi ZnO, ZnO/TiO_2 00.05 dan ZnO/TiO_2 didop dengan Fe^{3+} ialah masing-masing 130.57 nm, 150.68 nm 153.84 nm. Nilai E_{bg} saput tipis ZnO adalah dalam lingkungan 2.95 – 3.09 eV.

Introduction

Paraquat and malathion can be introduced into aquatic environments especially in the river through intentional application (controlling of aquatic weeds, algae, fish or unwanted invertebrates), aerial drift, runoff from agricultural applications or runoff from accidental release. Rivers are directly linked to estuaries, coasts and open seas where the pollutants can be transported by the flow, and contact with the atmosphere through volatilization [1].

Several methods were used in treating wastewater such as coagulation, photodegradation, ozonation, biological treatment, filteration, etc. The advantages of using photodegradation are, there are no sludge produced and foul

odors are greatly reduced, safety application of the reactions being performed at atmospheric pressure and near ambient temperature and requires only dissolved oxygen in water [2].

The molecular orbital of semiconductors has a band structure that consult highest occupied valence band and lowest unoccupied valence band separated by band gap energy, E_{bg}. When the semiconductor is illuminated with ultra violet light with photon energy greater or equal to the band gap energy of the semiconductor, valence band electrons are excited to the conduction band leaving a hole behind (Equation 1). TiO_2 anatase band gap energy is 3.2 eV while ZnO band gap energy is 3.17 eV. Superoxide anion radicals ($\bullet O_2^-$) and hydroxyl radicals (•OH) are being generated (Equation 2 and 3) in the aqueous medium and these spescies are responsible to accelerate the oxidation of pollutants [3, 4]. The efficiency of the photocatalysts activity can be enhanced by coupling the ZnO and TiO_2 (ZnO /TiO_2) semiconductor [5].

$$\text{Semiconductor} + h\nu \rightarrow e^- + h^+ \quad (1)$$
$$O_2 + e^- \rightarrow \bullet O_2^- \quad (2)$$
$$H_2O + h^+ \rightarrow \bullet OH + H^+ \quad (3)$$
$$OH^- + h^+ \rightarrow \bullet OH \quad (4)$$
$$\bullet OH + H^+ \rightarrow \bullet OH_2 \quad (5)$$

This research studies the degradation reaction of paraquat and malathion using single and couple semiconductor. The best ratio of TiO_2/ZnO coupled photocatalyst for both pesticides will then doped with Fe^{3+} ions. The photocatalyst was characterized further using X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) technique. The photodegradation was conducted in the presence of UV-light and monitored by UV-Visible spectroscopy and the mineralization was monitored using TOC analyzer. Degradation process is the process of breaking the organic molecules into smaller organic molecules, while mineralization process is a process that converts organic molecules into minerals such as NO_3^-, PO_4^{3-}, CO_3^{2-}, depending on the elements present in the molecule.

Experimental

Reagents and Chemicals

The commercial paraquat dichloride "Gramoxone PP910" with active ingredients 25 % w/w was purchased from CCMB Agrochemical Sdn. Bhd. Shah Alam. The standard paraquat (1,1'-dimethyl-4,4'-bipyridylium dichloride) was purchased from Reference Material for Residue Analysis, Germany, malathion (active ingredients about 57 % w/w), ferric nitrate nonahydrate ($Fe(NO_3)_3.9H_2O$ and ferrous sulfate heptahydrate ($FeSO_4.7H_2O$) were obtained from GCE (Goodrich Chemical and Emory). TiO_2 powder (99 % anatase, sigma), titanium tetraisopropoxide (TTIP), ethanol (absolute ≥ 99 %) and polyethylene glycol 2000 (PEG 2000), were obtained from Fluka Chemika while diethanolamine (DEA) from Riedel de Haen AG. Zinc acetate ($Zn(OAc)_2$) is obtained from Analar (BDH), and sodium hydroxide (NaOH) from Ashland Chemical and 2-propanol from J.T Baker.

Apparatus

Photocatalytic tests were performed in a batch photoreactor of 1000 mL made of pyrex glass cylinder. The calcination of the photocatalyst was carried out in the furnace Nabertherm L3/S17 model. Ultra violet lamp (Yamato, λ=354 nm, 6 W, 100 V) was used as the UV light sources with the support of a Teletron step down transformer (Model TSD 100 W). The instruments for monitoring and characterizing of samples are Perkin Elmer UV-Visible spectrophotometer, Shimadzu (TOC 500) Total Organic Carbon Analyzer, Siemens D5000 X-Ray diffractometer (XRD) equipped with Cu-K_α (λ=1.54 Å) radiation, Scanning Electron Microscopy (SEM Phillips XL 40), Ellipsometer Geatner and Shimadzu UV-3101PC UV-Vis-NIR Spectrophotometer.

Preparation of TiO_2 sol-gel

Polyethylene glycol (PEG 2000) (6 g) was dissolved in ethanol (600 mL) in a 1 L volumetric flask. The solution was stirred continuously until PEG was completely dissolved before 31.8 g diethanolamine (DEA) was added to the solution followed by 85.2 g of titanium(IV) isopropoxide (TTIP). The solution was left for a few minutes before 5.4 mL deionized water was added. The solution was stirred continuously for 3 hours at ambient temperature until it forms homogeneous solution. The conical flask was kept close during the sol-gel preparation to prevent the evaporation of ethanol as the process was exothermic [6].

Preparation of ZnO sol-gel
Zinc acetate (0.5 g) was dissolved in 2-propanol (100 mL) in a volumetric flask at 50-60°C and stirred continuously. At the same time, sodium hydroxide (NaOH) (10 mg) was dissolved in 2-propanol (100 mL) and stirred at the same temperature. These two solutions were mix together and continuously stirred in ice bath (at 0°C), then the solution was kept in water bath at room temperature for an hour [7].

Thin Film Preparation
The thin film was coated on glass support using the dip-withdraw method by repeating the dip-withdraw process for five times. The support used in this study is a microscope slide glass (76 x 26 x 2 mm). The coated slides were calcined in the furnace where the temperature was elevated at 1°C min^{-1} up to 550°C for TiO_2 photocatalyst and 2°C min^{-1} up to 500°C for ZnO and kept at this temperature for an hour [8].

Photocatalytic measurement
Photocatalytic study of TiO_2 and ZnO thin film was examined in degrading 200 mL pesticide solutions (1 x 10^{-4} M paraquat and 2 x 10^{-4} M malathion) under various experimental conditions. This photocatalytic reaction was carried out in a glass reactor and irradiated with UV lamp for 4 hours in the presence of photocatalyst. An aliquot (4 mL) was taken at specific time intervals. For the degradation process the samples were analyzed using UV-Vis spectrophotometer (Equation 6) and the Total Organic Carbon analyzer was used to analyze the mineralization of the pesticides (Equation 7).

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

where,
A_o= initial absorption
A_t= absorption at t time.

$$\% \text{ Mineralization} = (TOC_o/TOCt) \times 100 \quad (7)$$

Where,
TOC_o= total organic carbon value before irradiation
TOC_t= total organic carbon value after irradiation

Photodegradation using TiO_2, ZnO and a mixture of TiO_2/ZnO thin film
Seventeen microscope slide glasses containing TiO_2, ZnO and a mixture of TiO_2/ZnO (ratio 1:≤ 0.08) thin film as shown in Table 1 were used in paraquat and malathion degradation.

Photodegradation using the best photocatalyst doped with Fe^{3+}
The two best photocatalysts each for paraquat and malathion was doped with Fe^{3+} (ratio 1:0.005). 0.05062 g and 0.0035 g $Fe(NO_3)_3.9H_2O$ containing Fe^{3+} was weighed and added into 75 mL of the best TiO_2/ZnO and ZnO/TiO_2 sol-gel respectively and stirred. A clean microscope slide was dipped into the sol-gel and withdrew gently with a constant speed. The process was repeated for five times.

Table 1: Mixture ratios of TiO_2: ZnO (≤ 5%) and ZnO: TiO_2 (≤ 8%)

% Weight ratio TiO_2:ZnO (g)	TiO_2 sol-gel (mL)	ZnO sol- gel (mL)	Total sol-gel volume (mL)
1:0.05	30	43.75	73.75
1:0.03	40	35	75
1:0.01	60	17.5	77.5
0.08:1	80	0.22	80.22
0.05:1	80	0.14	80.14
0.03:1	80	0.07	80.07
0.01:1	80	0.03	80.03

Photodegradation using the best photocatalyst with Fe^{2+} ion dissolved into the working solution
20 mL of 55.84 ppm Fe^{2+} (9.998 x 10^{-5} M) ion solution was pipetted into 500 mL volumetric flask containing 200 mL pesticides and diluted with deionized water to make the working solution. The 200 mL working solution was place in a pyrex reaction cell and was treated as stated earlier in the photocatalytic measurement.

Effect of photocatalyst calcination temperature on the photodegradation process
The two best photocatalyst for each paraquat and malathion were calcined at different temperatures as shown in Table 2. The photocatalytic measurement was carried out as stated earlier.

Table 2: Calcination temperatures of the best photocatalyst

Number of slide	Calcination temperature (°C)	
	ZT03 (paraquat)	ZT05 (malathion)
2	600	600
2	200	200

ZT03: The best photocatalyst for paraquat, TiO_2 : 3% ZnO
ZT05: The best photocatalyst for malathion, ZnO : 5% TiO_2

Effect of support on photodegradation process
Prepared photocatalyst powder was weighed with the same amount of thin film coated onto the glass slide. Photocatalytic measurement was carried out as stated before using thin film and the prepared powder of the best photocatalyst.

Results and Discussions

Calibration of total organic carbon
A linear calibration curve was matched with UV absorption value in the same range in order to determine the suitable working solution concentration for further degradation process. The suitable concentration of formulated paraquat is 1 x 10^{-4} M (29.52 ppm) with UV absorption value, 1.363 and for formulated malathion, the suitable concentration is 2 x 10^{-4} M (59.89 ppm) with UV absorption value, 2.135.

Effect of TiO_2 thin film and commercial TiO_2 on paraquat and malathion photodegradation
Degradation and mineralization of paraquat with commercial TiO_2 was higher than TiO_2 thin film as shown in Figure 1 and Figure 2. 77.67% paraquat was mineralized by using commercial TiO_2 while only 42.21% was mineralized using prepared thin film. Commercial TiO_2 performed better as photocatalyst in which 58.57% malathion was degraded compared to 50.09% using TiO_2 thin film after 4 hours reaction. Mineralization process using commercial TiO_2 was better compared to TiO_2 thin film through out the reaction time due to the fact that commercial TiO_2 had a pure anatase crystal structure with high active surface area [9]. While the thin film catalysts prepared from the sol-gel method does not have a perfect lattice as the commercial catalyst thus giving a detrimental affect on their photocatalytic activity [10]. Even though the photocatalytic activity of commercial TiO_2 is better than the prepared thin film, the entire research was focused on the thin film photocatalyst to study the synergy effect of ZnO and TiO_2 semiconductor in degrading and mineralizing paraquat and malathion solution.

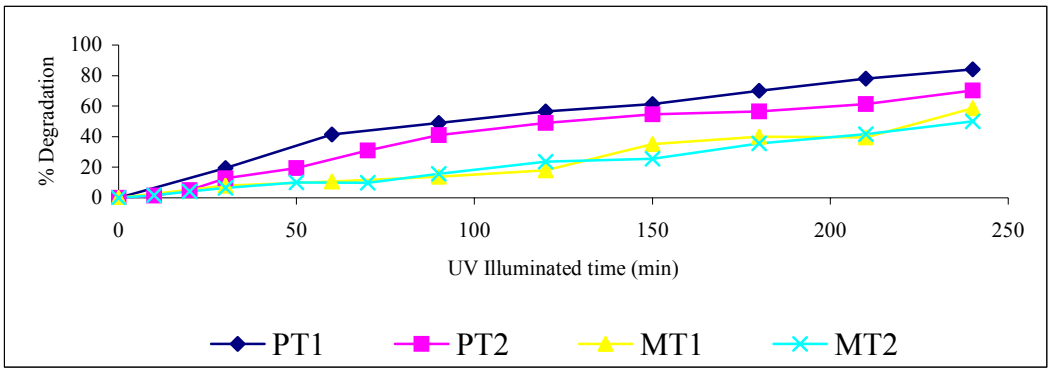


Figure 1: Percent degradation of paraquat (P) and malathion (M) at different illumination time. (PT1: commercial TiO_2 in paraquat, MT1: commercial TiO_2 in malathion, PT_2: TiO_2 thin film in paraquat and MT2: TiO_2 thin film in malathion).

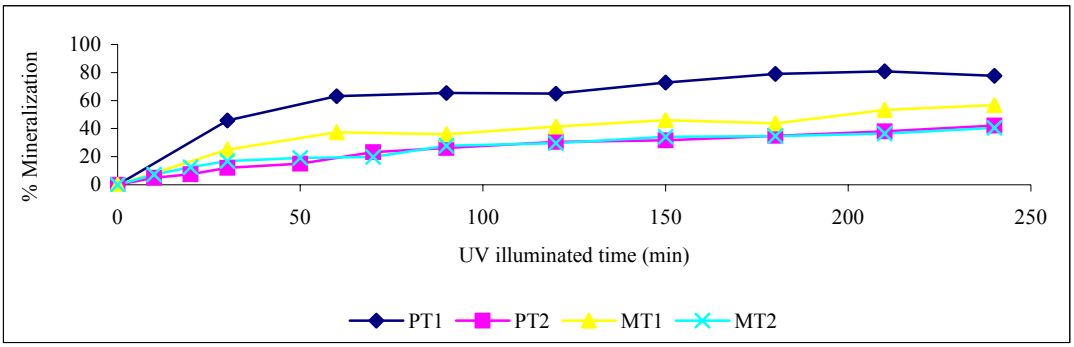


Figure 2: Percent mineralization of paraquat (P) and malathion (M) at different illumination time. (PT1: commercial TiO_2 in paraquat, MT1: commercial TiO_2 in malathion, PT_2: TiO_2 thin film in paraquat and MT2: TiO_2 thin film in malathion).

Effect of single TiO_2, ZnO and coupled TiO_2/ZnO semiconductor on paraquat and malathion photodegradation

The degradation and mineralization of paraquat were higher in the presence of TiO_2 photocatalyst than ZnO as shown in Figure 3. Modifying the surface properties of TiO_2 with ≤ 5% ZnO, significantly enhances the rate of photocatalytic degradation of this cationic pollutant. TiO_2/ZnO (TZ0.3; 1:0.03) couple semiconductor, containing 97% TiO_2 and 3% ZnO was chosen as the best photocatalyst in degrading paraquat solution (% degradation :80.12%, % mineralization: 52.32%). In contrast, the photodegradation of malathion was higher in the presence of ZnO as shown in Figure 4. The best photocatalyst in degrading malathion solution is zinc oxide couple with 0.05 titanium dioxide (95% ZnO and 5% TiO_2). The optimum degradation of malathion is 84.92% while the total mineralization is 58.66% after 4 hours reaction.

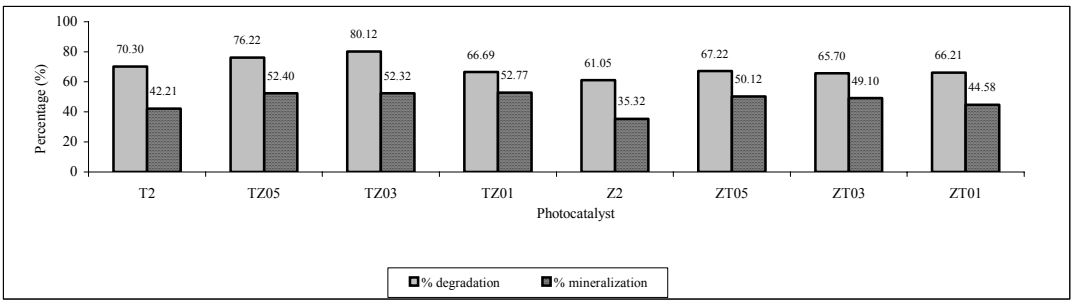


Figure 3: Percent of degradation and mineralization of paraquat with single and couple semiconductor photocatalyst TiO_2 and ZnO after 4 hours UV radiation.

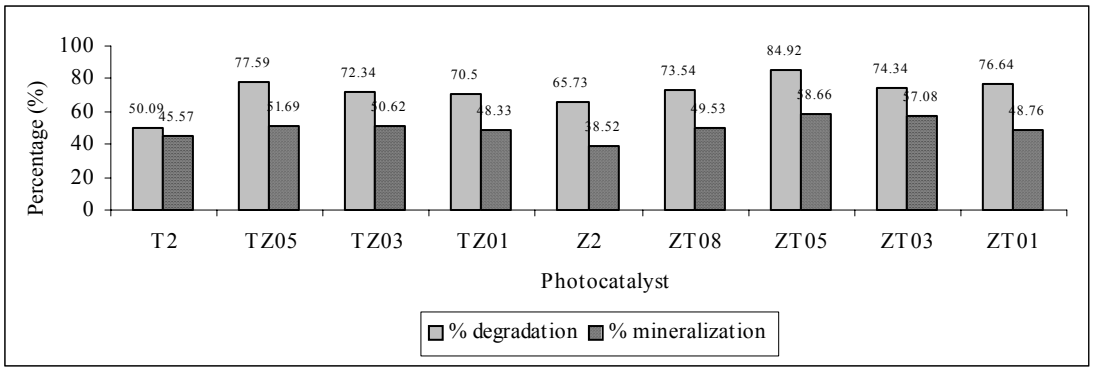


Figure 4: Percent of degradation and mineralization of malathion with single and couple semiconductor photocatalyst TiO_2 and ZnO under UV light within 4 hours reaction.

Effect of Fe^{3+} as dopant (co-catalyst) and the addition of Fe^{2+} ions into the working solution.
Theoretically, the presence of metal ions can delay the recombination process of generated electrons and holes as shown in Equation 8 and 9. Therefore the photodegeadation results are expected to be higher. 92.71% total degradation and 77.07% total mineralization of paraquat while 94.74% degradation and 81.17% mineralization of malathion were observed when Fe^{2+} ion was added into the pesticide solution after 4 hours illumination as shown in Figure 5 and Figure 6.

$$M^{n+} + e \rightarrow M^{(n-1)+} \quad (8)$$
$$M^{(n-1)+} + h^{+} \rightarrow M^{n+} \quad (9)$$

In contrast, the use of Fe^{3+} as dopant gave detrimental effect. When the metal is deposited on the photocatalyst, it was scattered in the bulk of the catalyst therefore increasing the recombination process of $e^{-}h^{+}$ pairs.

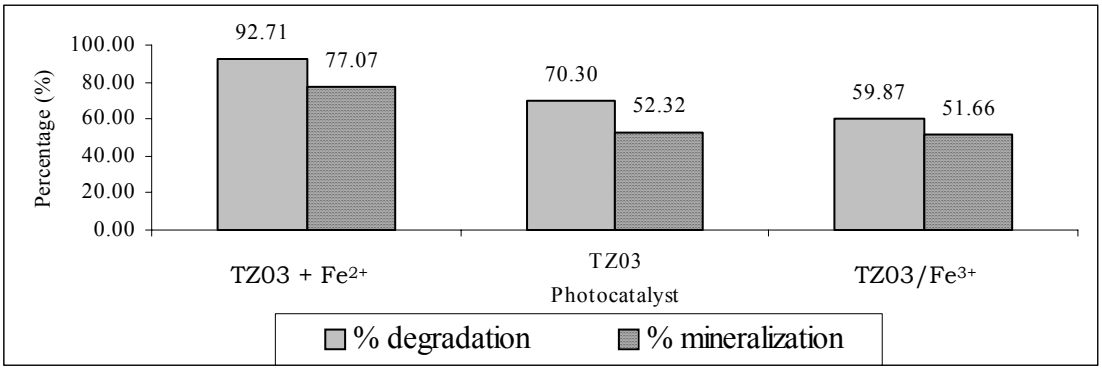


Figure 5: Percent of degradation and mineralization of paraquat with the best of photocatalyst doping with Fe^{3+} ($TZ03/Fe^{3+}$) and the addition of Fe^{2+} into paraquat solution ($TZ03 + Fe^{2+}$).

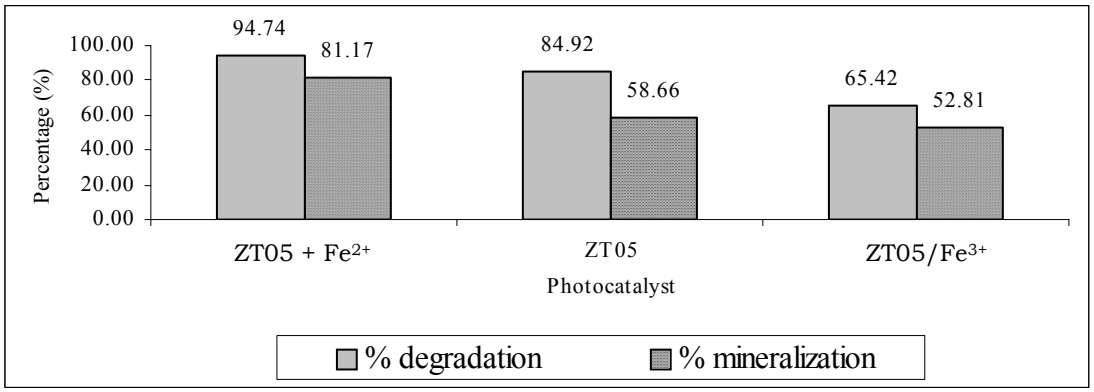


Figure 6: Percent degradation and mineralization of malathion with the best of photocatalyst doped with Fe^{3+} ($ZT05/Fe^{3+}$) and the addition of Fe^{2+} into the malathion solution ($ZT05 + Fe^{2+}$).

Effect of calcinations temperature.
The optimum degradation was observed with catalyst calcined at 550°C. 80.12% paraquat was degraded at this temperature compared to 600°C (48.01%) and 200°C (21.36%) as shown in Figure 7. A similar pattern was observed for mineralization. Catalyst prepared at 550°C gave the highest percent of mineralization followed by 600°C and 200°C. The amorphous titania is known to have very low photocatalytic activity compared to that of the anatase or rutile phase due to an increased of electron – hole pairs recombination rate [11]. At 550°C the anatase phase is fully formed while at a temperature of 600°C, the rutile phase starts to appear. Anatase phase has a high photocatalytic activity because it contain more surface hydroxyl group that can react with holes to generate hydroxyl radicals. The recombination process was thus delayed by the presence of hydroxyl radical.

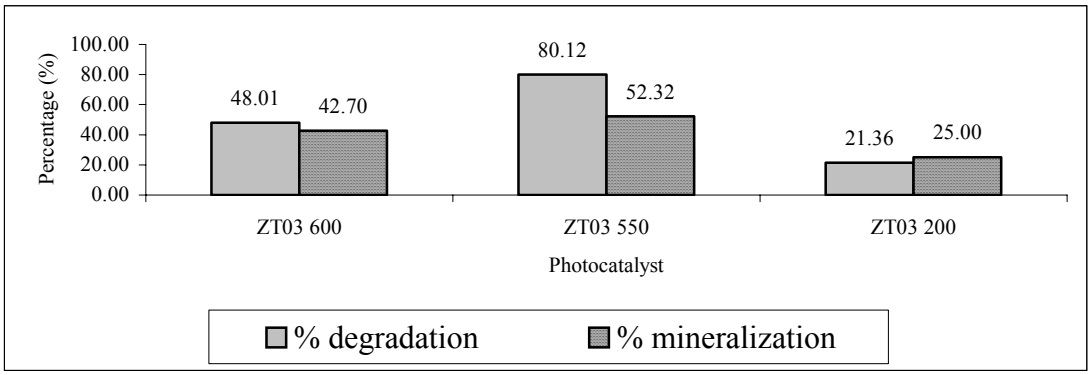


Figure 7: Percent degradation and mineralization of paraquat with the best of photocatalyst with various calcinations temperature (TZ03 600: 600°C, TZ03 550: 550°C, TZ03 200: 200°C)

From Figure 8, the optimum degradation (80.12%) and mineralization (52.32%) were observed using catalyst calcined at 500°C. At this temperature, the ZnO wurtzite crystal has fully formed [12]. At 600°C, the percentage of the degradation and mineralization of the pesticide decreases. Agglomeration of the photocatalyst will occur which attributed to the low surface area. This condition will lower the photocatalytic activity of the photocatalyst. While at 200°C, crystallization of crystalline ZnO is incomplete.

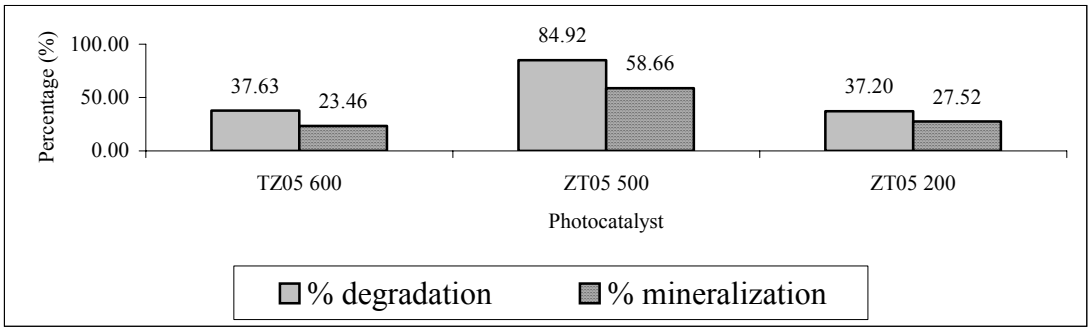


Figure 8: Percent of degradation and mineralization of malathion with the best of photocatalyst with various calcinations temperature (ZT05 600: 600°C, ZT05 500: 500°C, ZT05 200: 200°C)

Supported photocatalyst

The catalyst coated on support were observed to perform better than the powder (unsupported) as shown in Figure 9 and Figure 10. The greater substrate degradation and mineralization is due to the availability of surface adsorption site in the prepared thin film. Catalyst activity of the unsupported photocatalyst was lower because the catalyst particles were trapped inside the agglomeration particle where radiation cannot penetrate. This will avoid the maximum generation of electron and hole pairs.

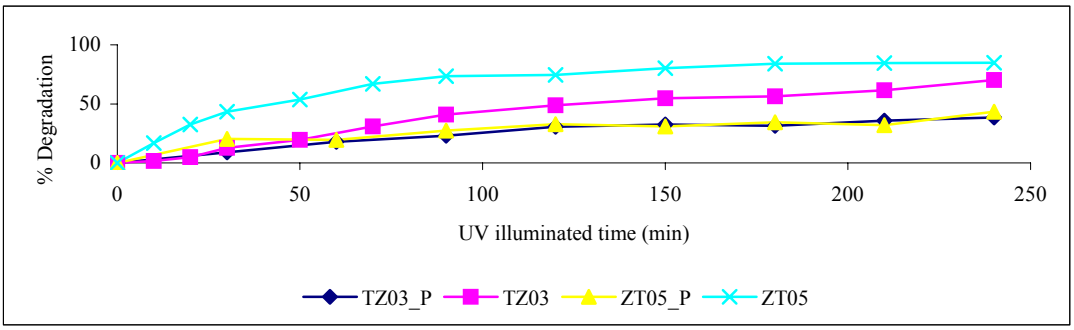


Figure 9: Percent degradation of pesticide with the best photocatalyst thin film (TZ03) and powder form (TZ03_P) for paraquat and the best photocatalyst thin film (ZT05) and powder form (ZT05_P) for malathion.

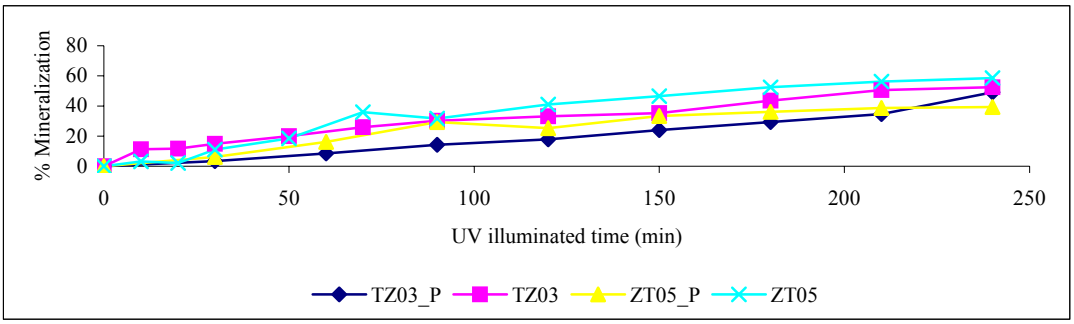
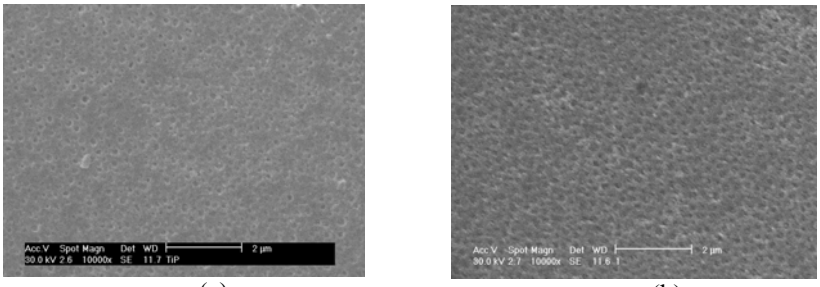


Figure 10: Percent mineralization of pesticide with the best photocatalyst thin film (TZ03) and powder form (TZ03_P) for paraquat and the best photocatalyst thin film (ZT05) and powder form (ZT05_P) for malathion.

SEM analysis

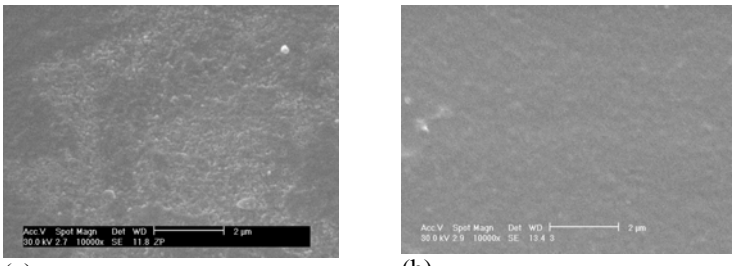
As shown in Figure 11, TiO_2 thin films were mainly composed of small uniform spherical particles monodispersed on the surface of the glass slide with a calcination temperature of 550°C. The surface of the films exhibited a certain degree of roughness and the thin film become rougher when coupled with zinc oxide.



(a) (b)

Figure 11**:** SEM micrographs of a) TiO_2 thin film b) TiO_2/ZnO 0.03 couple semiconductor thin film calcined at 550°C (magnification factor: 10000x)

The SEM micrographs for ZnO photocatalyst calcined at the same temperature of 500°C is shown in Figure 12 which indicates the irregular shape of particle formed. The second thin film, which was couple with 5%, TiO_2 shows smooth surface with a fine microstructure without cracks and voids. The grains of the film become larger and denser if coupled with TiO_2.



(a) (b)

Figure 12: SEM micrographs of a) ZnO thin film b) ZnO/TiO_2 0.05 couple semiconductor thin film calcined at 500°C (magnification factor: 10000x).

XRD analysis

Diffractogram of catalyst calcined at 200°C indicated that the catalyst was an amorphous phase as shown in Figure 13. By increasing the temperature up to 450°C, transformation of phase occurred whereby amorphous phase was transformed to anatase phase. At 600°C, the rutile phase started to appear, therefore forming a mixture of anatase and rutile catalyst. The presence of rutile phase will decrease the performance of catalyst due to the lack of hydroxyl ion surface species. Thus will increased the (e^- - h^+) pairs recombination process.

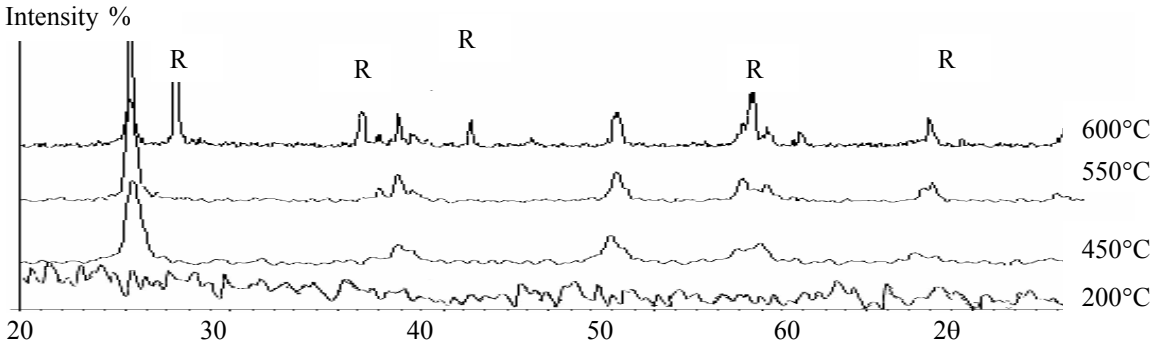


Figure 13: Diffractograms of TiO_2/ZnO 0.03 prepared using sol-gel method and calcined at 200°C, 450°C, 550°C and 600°C (R=rutile).

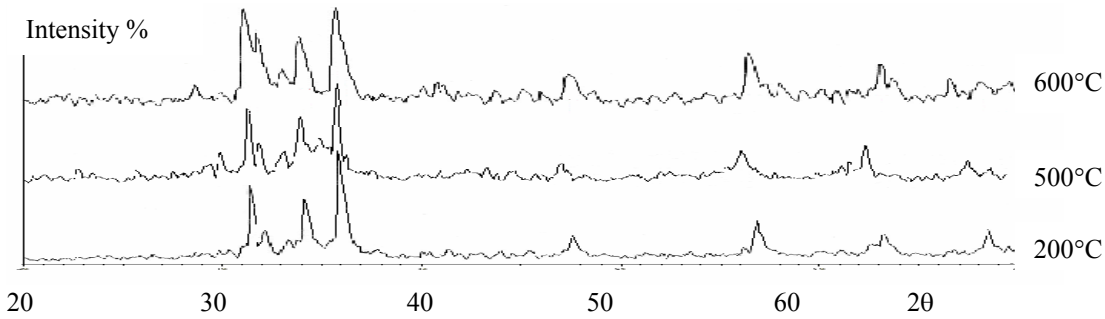


Figure 14: Diffractograms of ZnO/TiO_2 0.05 prepared using sol-gel method and calcined at 200°C, 500°C and 600°C.

By increasing the calcinations temperature of ZnO photocatalyst to 500°C, the increment of intensity become stronger, which indicated that the quality of ZnO catalyst in thin film has improved as shown in Figure 14. At 200°C, the formation of the metastable ZnO phase occurred. This was supported by Yang *et. al.* [13] who reported that low temperature portion of the ZnO-TiO_2 phase diagram is difficult to study due to the sluggishness of the reactions and the similarities of the XRD patterns.

Ellipsometer (Thickness measurement)

The values of polarizer (P), analyzer (A), thickness and refractive index of the thin film photocatalyst are shown in Table 3. The thickness of the thin film increases as it was coupled with different semiconductor and doped with Fe^{3+} ions. As the second semiconductor and metal ion were added, the viscosity of the sol-gel increased.

Table 3: The angle value of polarizer (P), analyzer (A) and the value of thickness and refractive index of the thin film photocatalyst.

Parameter	**Angle value for thin film (°)**		
	ZnO	**ZnO/TiO_2 0.05**	**ZnO/TiO_2 0.05/Fe^{3+}**
A_1	22.9	18.8	24.3
P_1	130.4	128.0	127.3
A_2	149.2	158.5	154.7
P_2	199.8	214.4	218.2
Thickness (nm)	**130.57**	**150.68**	**153.84**
Refractive Index	**2.4946**	**2.1984**	**2.2042**

UV-Vis-NIR analysis (Band gap Energy measurement)

The band gap energy, E_{bg} values for all thin films were determined by plotting $[\alpha hc/\lambda]^{1/2}$ versus the equivalent energy at wavelength λ (h = Planck constant, c = light velocity). The α (absorption coefficient) was derived from the measured transmittance (T) and reflectance (R) factors with a wavelength ranging from 300-500 nm. The α can be obtained by using the following relationship:

$$T = (1-R^2) \exp(-\alpha d) \quad (10)$$

Where d is the thickness of the thin film. The resulting diagram is called Tauc's plot (Figure 15) and the respective band gap energy was obtained by extrapolation of the Tauc plot dataset to $[\alpha hc/\lambda]^{1/2} = 0$. Coupled TiO_2 have the lowest bandgap energy (2.95 eV) than single ZnO photocatalyst (3.04 eV). Band gap energy for doped catalyst was higher (3.09 eV) than coupled TiO_2. These data were in a good agreement with the results obtained in the photodegradation reaction data. The higher value of E_{bg} will reduce the formation of (e^-- h^+) pair, therefore reducing the performance of the photocatalyst.

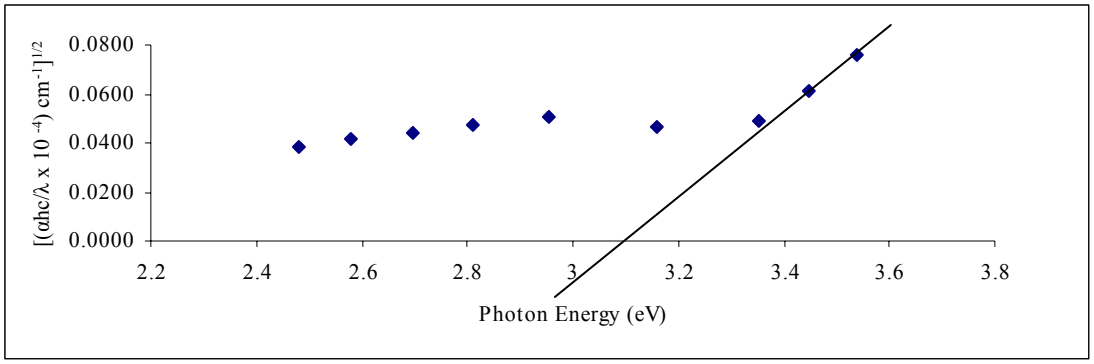


Figure 15: Tauc's plot for indirect band gap of ZnO (E_{bg}: 3.04 eV)

Conclusion

Zinc oxide is an efficient catalyst in degrading malathion solution while titanium dioxide is found to be more efficient in degrading paraquat solution. The best coupled photocatalyst degrading malathion solution is ZnO:TiO_2 with a ratio of 1:0.05. In contrast the best coupled photocatalyst in degrading paraquat solution is TiO_2:ZnO in a ratio of 1:0.03. Dissolved Fe^{2+} ions have showed the highest photocatalytic activity in degrading paraquat and malathion solution. Coupled photocatalyst doped with Fe^{3+} ion exhibited lower photodegradation compared to undoped coupled photocatalyst. The best calcination temperature for TiO_2 based photocatalyst is 550°C while for ZnO based photocatalyst is 500°C. This result was supported by XRD diffractograms and SEM micrographs. Supported catalyst plays an important role giving the high dispersion rate and enhanced the photodegradation process of paraquat and malathion rather than the unsupported one. The thickness of ZnO, ZnO/TiO_2 0.05 and ZnO/TiO_2 0.05 doped with Fe^{3+} thin film are 130.57 nm, 150.68 nm and 153.84 nm. The band gap energy values measured using UV-Vis NIR are in the range of 2.95 – 3.09 eV.

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