Jurnal Teknologi, 47(C) Dis. 2007: 1–8

TIO_2 AND ZNO ON DIFFERENT SUPPORTS FOR PHOTODEGRADATION OF PARAQUAT

NORAIDURA AMIN[1], RUSMIDAH ALI[2], WAN AZELEE WAN ABU BAKAR[3], MOHD NORDIN GARIF[4] & MOHD. YUSUF OTHMAN[5]

Abstract: Paraquat dichloride has been extensively used as herbicide and the residual in the environment is known for its potential health hazard. The contaminant is non-biodegradable, toxic, stable and persistent in the environment. In this study, the photocatalytic activity of TiO_2 and ZnO immobilized on different supports (cement and tile) were studied to treat this pollutant. The catalysts were prepared by two different techniques, namely, slurry method on tile and powdered scattering on cement. The degradation of paraquat was carried out in photocatalytic reactor using ultraviolet (UV) lamp at wavelength of 354 nm as a light source. The sample was illuminated for five hours. The disappearance of paraquat in the photodegradation process was monitored by UV-Vis spectrophotometer at the 400 – 200 nm region. Experiment in a dark condition and using support without catalyst was conducted as comparison control. Experimental results showed that both illumination and the catalyst were necessary for the degradation of the contaminant substrate. The data indicated that ZnO on tile is the best catalyst which 63.42% degradation was recorded compared to TiO_2 on tile that was only 22.09% of degradation. Therefore, ZnO is a low cost alternative photocatalyst potential to be used for the degradation of paraquat.

Keywords: Photodegradation; support; titanium dioxide; zinc oxide; paraquat dichloride

Abstrak. Parakuat diklorida telah digunakan dengan meluas sebagai racun rumpai dan bahan sisanya dalam persekitaran boleh mendatangkan risiko terhadap kesihatan. Bahan pencemar ini biasanya tidak terbiodegradasi, toksik dan stabil dalam sekitaran. Dalam kajian ini, aktiviti pemangkinan TiO_2 dan ZnO yang dipegun di atas penyokong yang berbeza (simen dan jubin) dikaji untuk merawat bahan pencemar ini. Mangkin disediakan melalui pelbagai teknik seperti kaedah larutan pekat ke atas jubin dan penaburan serbuk mangkin ke atas simen. Proses degradasi terhadap parakuat dilakukan di dalam reaktor pemangkinanfoto menggunakan lampu ultralembayung dengan panjang gelombang 354 nm sebagai sumber cahaya. Sampel disinarkan selama lima jam. Pelenyapan parakuat dalam proses degradasifoto dipantau menggunakan spektrofotometer UV-Vis pada julat panjang gelombang 400 – 200 nm. Eksperimen ini juga dilakukan dalam keadaan gelap dan menggunakan penyokong tanpa mangkin sebagai perbandingan. Hasil kajian menunjukkan kedua-dua sinaran dan mangkin diperlukan dalam proses degradasi bahan pencemar. Data yang diperolehi mendapati ZnO yang disokong di atas jubin adalah mangkin yang terbaik di mana sebanyak 63.42% direkod berbanding hanya 22.09% TiO_2 yang disokong di atas jubin. Oleh itu, ZnO boleh digunakan sebagai mangkin alternatif berkos rendah untuk degradasi parakuat.

Kata kunci: Degradasifoto; titanium dioksida; zink oksida; parakuat diklorida

[1,2,3,4&5] Chemistry Department, Faculty of Science, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor Bahru, Malaysia

1.0 INTRODUCTION

Polluted water caused by hazardous materials is a serious problem globally. Persistent contaminants include pesticides, solvents, amines, detergents and a variety of industrial chemicals has due to the combination of its chemical stability and resistance to biodegradation. Since the contaminants are difficult to decompose by biodegradation through bacteria, they accumulate in nature and persist for a long time. For example, the large amount of amines used in petroleum refinery to remove CO_2 and H_2S cause contamination to the quality of environmental water. Photocatalysis is one of the most interesting processes in elimination of organic pollutants in water, because it is a clean technology in water treatment system and the final decomposition products of organic compounds are only CO_2, water and mineralization products.

Among the photocatalysts, TiO_2 is the most widely used for purifying and treating water. The strong oxidative power of photogenerated holes on the TiO_2 surface has made it the most practical photocatalytic material in the fields such as environmental remediation [1]. TiO_2 has been widely used as a photocatalyst because of its effective, easily available, relatively inexpensive [2], chemically and physically stable, non-toxic, and low cost [3 – 4].

However in other studies showed that another metal oxide, ZnO is known to be photoactive oxides under solar irradiation and their photodegradation mechanisms have been proven to be similar to that of TiO_2, although they exhibit less vigorous oxidation states [5 – 8]. ZnO absorbs over a larger fraction of solar spectrum than TiO_2, therefore shows the highest percentage of azo dye decolourization compared to TiO_2 and WO_3 [9]. Avranas *et al.* [5], observed that the degradation rate is almost identical for TiO_2 and ZnO in degrading cationic surfactant dodecylpyridinum chloride.

Most of the studies related to photodegradation reactions have been carried out using suspension of TiO_2 and ZnO powder. However, the removal from water is difficult and recent research has focused on the preparation of immobilized catalysts for water treatment. Pal and Sharon [10] investigated on highly porous ZnO thin film prepared by sol-gel process. These films have been found to decompose aqueous solutions of phenol, chlorophenol, naphthalene and anthracene to CO_2 efficiently. Fernandez *et al.* [11] had investigated the degradation of malic acid using TiO_2 photocatalysts supported on various rigid supports such as glass, quartz and stainless steel. Pozzo *et al.* [12] have made an overview of the research on supported titanium oxide as photocatalyst. Since the powder form usually gives better performance [13] than the immobilized thin films, therefore an alternative has to be developed to improve the immobilized catalysts.

The aim of the present work is to investigate the performance of the TiO_2 and ZnO powder supported on the various supports for the degradation of paraquat. Cement and tile will be used to immobilize the catalyst as support.

2.0 EXPERIMENTAL

2.1 Photocatalyst

The catalysts used were ZnO grade material 99% purity (Emory) and TiO_2 of 99% purity (Sigma). Both were used without any further treatment. The cement supported catalyst were produced using powder scattering method whereby a certain amount of catalyst powder (0.2 g) were scattered evenly on the surface of the wet cement that was coated on a glass slide as its base. It was then left to dry for a day.

The tile supported catalyst was produced using slurry method whereby the specific amount of catalyst was formed into a paste by a few drops of distilled water. It was then poured onto the tiles and spread evenly using a glass rod and turned upside-down to form homogeneous slurry on the support.

2.2 Photocatalytic Activity

The experimental setup consists of a UV lamp (100 volt, 6 W) with 354 nm of wavelength as the light source. The supported catalyst was dipped into the paraquat solution (150 mL). The sample was then illuminated for five hours and 5 mL of sample was taken out every hour. The collected sample was then sent to UV/Vis to obtain the percentage of degradation by the declining of absorbance of paraquat peaks at 258 nm as shown in Equation 1.

$$\text{Percent of Degradation} = \frac{(A_0 - A_t)}{A_t} \times 100 \tag{1}$$

Where

A_0 = initial absorption

A_t = absorption at t minute.

2.3 Support

Cement used in this experiment was Portland cement. Tile used was ceramic bare tile: polished surface has been removed by grinding.

3.0 RESULTS AND DISCUSSION

The results of the study are discussed in term of the percentage of paraquat degradation per hour of testing. The percentage of degradation was evaluated by monitoring the relative reduction of the maximum absorbance (λ_{max} = 258 nm) as shown in Equation 1.

In Figures 1 and 2, the percentage of paraquat degradation using cement and tile as support, respectively, at fixed reaction time (5 hours) is shown. For both supports

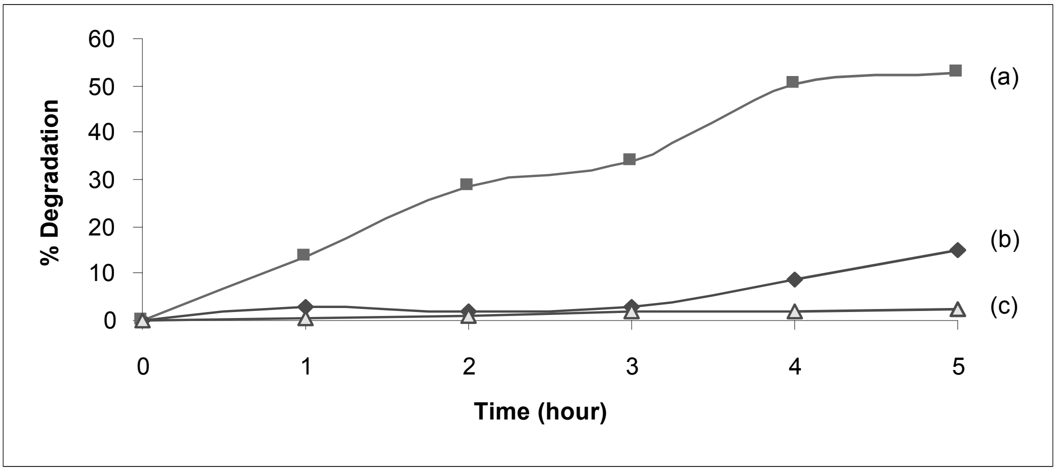


Figure 1 Percentage degradation of paraquat for cement supported (a) ZnO, (b) TiO_2 and (c) cement after irradiation with UV light, 354 nm

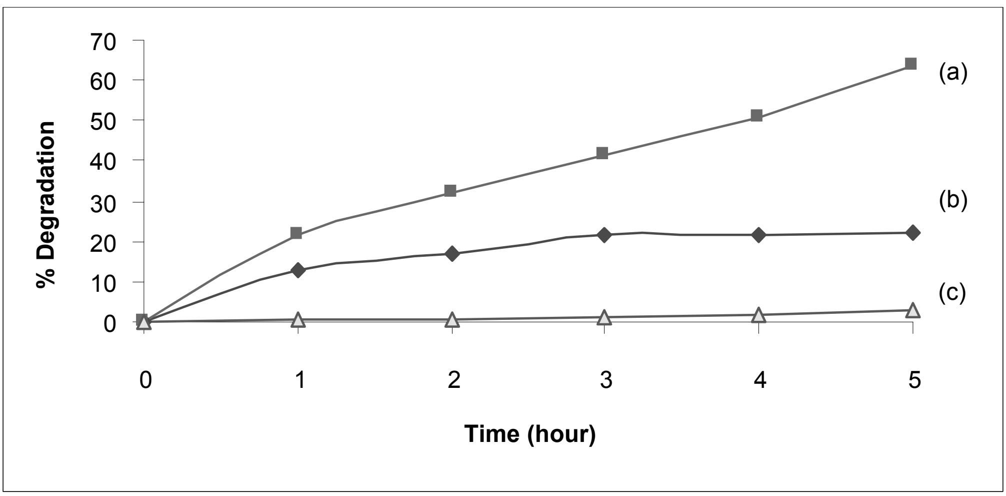


Figure 2 Percentage degradation of paraquat for tile supported (a) ZnO, (b) TiO_2 and (c) tile after irradiation with UV light 354 nm

without catalyst, the experimental data show that it is not reactive towards paraquat, and thus did not show any chemical degradation or absorption. On the other hand, as TiO_2 was coated on both supports, the tile supported TiO_2 did show an increase in degradation up to 22.09% after 5 hours. However, cement supported TiO_2 only showed a slight increase of 15.09% after 5 hours irradiation time. Meanwhile both of the support that has been coated by ZnO showed tremendous results as the degradation increase to a high of 52.75% for cement support ZnO, and 63.42% for tile supported ZnO.

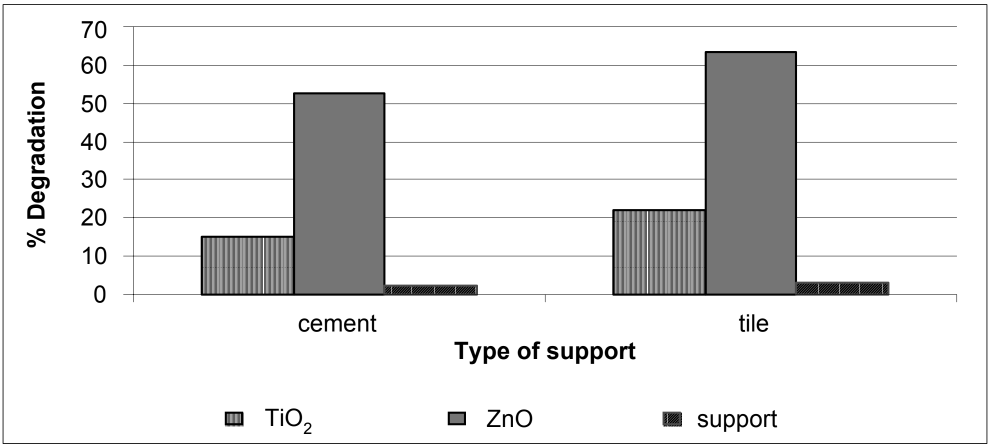


Figure 3 Comparison of supports efficiency for supported TiO_2 and ZnO, over degradation of paraquat after 5 hours illumination using UV light, 354 nm

The comparison of support efficiency for TiO_2 and ZnO, on cement and tile is shown in Figure 3. The catalyst supported on tile serves better for the degradation of paraquat with degradation using TiO_2 on tile accomplished at 22.09% degradation compared to 15.09% supported on cement, while ZnO on tile degraded 63.42% paraquat compared to the former 52.75% using cement. This was presumably due to the different methods in catalyst coating on support. Powder scattering method on cement resulted in the build-up of layers of the catalyst powder on the support resulting in small surface area and small pores for the catalyst to degrade paraquat. Though this method gives a homogeneous effect in the eye view, but as the supported catalyst was dipped in paraquat solution, it is either the powder peeled off from the support that makes the catalyst cannot be used any longer, or the surface area was too small for paraquat to be degraded. To avoid the peeling of the catalyst, the use of other polymeric materials as binder is suggested in order to extend the performances of the photocatalyst and stable for repeated use. Meanwhile the slurry method that was used to coat the catalyst on the tiles gave larger catalyst surface area as it was homogeneously distributed by the paste, as shown in SEM micrograph in Figure 5b.

Comparison of the supported and unsupported catalysts is shown in Figure 4. Degradation using unsupported catalyst was conducted for comparison purpose and TiO_2 showed superiority compared to ZnO with 81.15% degradation of paraquat compared to 56.13% respectively. However, when both catalysts were coated onto the support, TiO_2 showed extreme reduction in its capability to degrade paraquat but not for ZnO.

Both of the supported TiO_2 catalysts showed only 15.09% (cement) and 22.09% (tile) degradation of paraquat. This shows that though TiO_2 has high catalytic activity on its own, the catalyst efficiency drastically declined as soon as it was coated to a

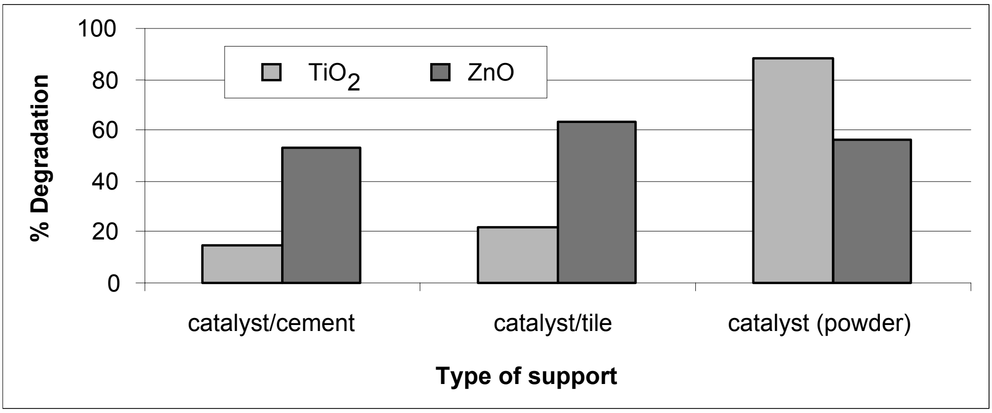
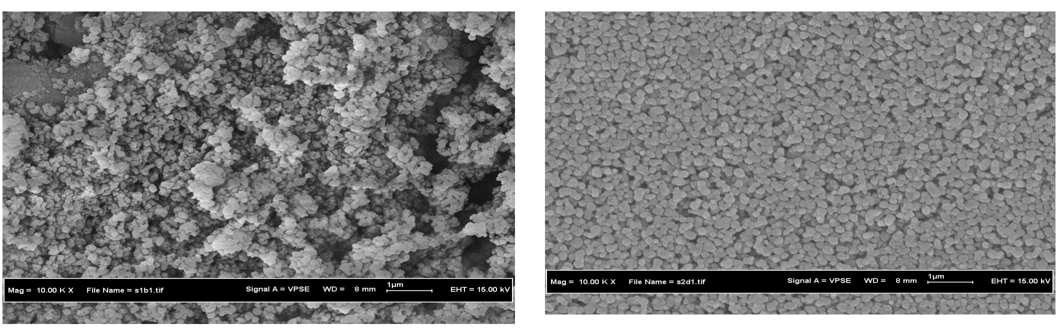


Figure 4 Comparison of catalyst efficiency for TiO_2 and ZnO catalyst, without and using cement and tile as support over degradation of paraquat using UV light, 354 nm

support. Meanwhile though ZnO alone has low degradation, its capability increases to 52.75% (cement) and 63.42% (tile), which means that it can be implemented in real life. This finding is in a good agreement with Kandavelu *et al.* [7] who investigated photocatalytic degradation of isothiazolin-3-ones in water and emulsion paints containing nanocrystalline TiO_2 and ZnO catalysts. They found out that ZnO exhibits comparable activity with TiO_2 and in some cases it was found to be even better than TiO_2.

Figure 5 shows the FESEM surface morphology studied by using field emission scanning electron microscopy. The FESEM micrographs showed that the catalyst supported on the tile form small particles in uniform size, highly disperse and homogeneously distributed on the surface. It would give larger surface area for photocatalytic activity. However, the FESEM micrograph for cement-supported catalyst indicates that the surface particles was aggregated, non-uniform and not



(a) (b)

Figure 5 FESEM micrographs of (a) TiO_2 immobilized on cement (b) TiO_2 immobilized on tile properly dispersed. These results justified the superiority of using tile as support compared to cement.

4.0 CONCLUSION

The results presented in this paper indicated that method of catalyst preparation plays an important role in determining the efficiency of the catalyst. Slurry method was proven to be better than powder scattering method, in particle size, homogeneity, and life span of the catalyst. The most efficient support is tile, as it gave larger surface area to many pores. The most efficient catalyst is ZnO supported on tile catalyst as it gave the highest percentage of paraquat degradation, however, the efficiency is still lower than the powder form of TiO_2.

ACKNOWLEDGEMENT

The authors thank MOSTI for financial support (vote 74248) and UTM for other supports.

REFERENCES

[1] Yu, D., R. Cai and Z. Liu. 2004. Studies on the Photodegradation of Rhodamine Dyes on Nanometer-Sized Zinc Oxide. *Spec. Act. Part A*. 60: 1617-1624.

[2] Özkan, A., M. H. Özkan, R. Gürkan, M. Akçay and M. Sökmen. 2004. Photocatalytic Degradation of a Textile Azo Dye, Sirius Gelb GC on TiO_2 or Ag-TiO_2 Particles in the Absebce and Presence of UV Irradiation: The Effects of Some Inorganic Anions on the Photocatalysis. *J. Photochem. and Photobio A: Chem*. 163: 29-35.

[3] Chhor, K., C. Bocquet and C. Justin. 2004. Comparative Studies of Phenol and Salicylic Acid Photocatalytic Degradation: Influence of Absorbed Oxygen. *Mat. Chem. & Phys*. 86: 123-131.

[4] Sun, R. D., A. Nakajima, T. Watanabe and K. Hashimoto. 2003. Decomposition og Gas-Phase Octamethyltrisiloxane on TiO_2 Thin Film Photocatalysts-Catalytic Activity, Deactivation and Regeneration. *J. Photochem. and Photobio A: Chem*. 154: 203-209.

[5] Avranas, A., G. Kyriakou, I. Poulios, C. Kypri and D. Jannakoudakis. 1993. Heterogeneous Photocatalytic Degradation of the Cationic Surfactant Dodecylpyridium Chloride. *Apl. Catal. B:Enviromental*. 289.

[6] Dindar, B. and S. Icli. 2001. Unusual Photoreactivity of Zinc Oxide Irradiated by Concentrated Sunlight. *J. of Photochem. And Photobiol. A: Chemistry*. 140: 263.

[7] Kandavelu, V., H. Kastien and K. R. Thampi. 2004. Photocatalytic Degradation of Isothiazolin-3-ones in Water and Emulsion Paints Containing Nanocrystalline TiO_2 and ZnO catalysts. 48: 101.

[8] Richard, C., P. Boule and J. M. Aubry. 1991. Oxidizing Species Involved in Photocatalytic Transformations on Zinc Oxide. *J. Photochem. and Photobio A: Chem*. 60(2): 235.

[9] Sakthivel, S., B. Neppolian, M. V. Shankar, B. Arabindoo, M. Palanichamy and M. Murugesan. 2003. Solar Photocatalytic Degradation of Azo Dye: Comparison of Photocatalytic Efficiency of ZnO and TiO_2. *Solar Energy Material and Solar Cells*. 77: 65-82.

[10] Pal. B. and M. Sharon. 2002. Enhanced Photocatalytic Activity of Highly Porous ZnO Thin Films Prepared by Sol-gel Process. *Mat. Chem. and Phys.* 76: 82.

[11] Fernandez, A., G. Lassaletta, V. M. Jimenez, A. Justo, A. R. Gonzalez-Elipe, J. M. Hermann, H. Tahiri and Y. Ait-Ichou. 1995. Preparation and Characterization of TiO_2 Photocatalysts Supported on Various Rigid Supports (Glass, Quartz and Stainless Steel). Comparative Studies of Photocatalytic Cctivity in Water Purification. *Appl. Catal. B:Environmental.* 7: 49.

[12] Pozzo, R. L., M. A. Baltanas, and A. E. Cassano. 1997. Supported Ttitanium Oxide as Photocatalyst in Water Decontamination: State of the Art. *Catal.Today*. 39: 219.

[13] Subramaniam, G. 2002. *The Optimizing of Photocatalytic Degradation of Paraquat using Titanium(IV) Oxide Thin Film*. Master Thesis. Universiti Teknologi Malaysia. 102.