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SOLAR PHOTOCATALYTIC DECONTAMINATION AND DISINFECTION OF WATER

RINGKASAN: *Fotopemangkinan menggunakan TiO_2 untuk menyahtosikkan air yang tercemar merupakan kajian yang paling luas dijalankan dan dibangunkan pada hari ini untuk aplikasi yang praktikal dalam rawatan air pencemaran. Rawatan fotopemangkinan berguna untuk merawat bahan-bahan merbahaya seperti fenol, sisa pertanian, racun perosak dan lain-lain. Objektif kajian ini adalah untuk menunjukkan kebolehan proses fotopemangkinan dalam menyahtosik air yang dicemari oleh racun perosak. Prestasi kemusnahan fotopemangkinan racun perosak tercemar air bawah tanah telah dikaji pada skala perintis dengan menggunakan fotomangkin TiO_2. Kajian ini menunjukkan bahawa 80 % dan 54 % penguraian telah dicapai selepas 24 jam melalui sinaran UV dan solar.*

ABSTRACT: Photocatalysis using TiO_2 for detoxification of contaminated water is most extensively been studied and developed today as of its practical applications to treat water contaminants. Photocatalytic treatment can be useful for addressing hazardous contaminants such as phenols, agricultural wastes, pesticides and etc. The objective of this study was to demonstrate whether detoxification of pesticide contaminated water by TiO_2 photocatalysis process is possible. The performance of photocatalytic degradation of pesticide contaminated groundwater has been studied at pilot scale with the TiO_2 photocatalyst. The study showed that 80 % and 54 % mineralization has been attained after 24 hours of UV and solar radiation, respectively.

Keywords: Photocatalytic treatment, UV, solar, TiO_2

INTRODUCTION

Photocatalytic technology is one of the most promising methods applied to treat the environmental pollutants. Photocatalytic technology evolves around the irradiation of photocatalysts to create powerful oxidation reactions that will, among the many applications, degrade organic pollutants to carbon dioxide, and also to disinfect microbial.

Photocatalytic treatment of contaminated water is clearly the most successful photochemical application of solar photons. Particularly, heterogeneous titanium dioxide (TiO_2) photocatalysis is the process for which the solar technology is the most extensively studied and developed to treat water contaminants (Blanco & Malato, 2010). The photocatalytic process can be applied to hazardous non-biodegradable contaminants, with difficult conventional treatment, in the range of several hundred mg/L of maximum organic concentration. It also extends to complex mixtures of organic contaminants. Thus, the photocatalytic technology can be considered useful for addressing hazardous contaminants such as phenols, agrochemical wastes, halogenated hydrocarbons, biocide compounds from pharmaceutical industry, wood preserving waste and etc.

Purification of contaminated groundwater is a challenging task. (Lim *et al.*, 2010). For some recalcitrant contaminants, the conventional treatment technologies are either slow or do not decompose the contaminant in-situ. Photocatalysis is an environmentally friendly process in which the photocatalyst such as titanium dioxide is a non-toxic material and the reaction degrades a wide range of organic compounds to carbon dioxide, water and mineral acids (Hoffmann *et al.*, 1995). TiO_2 has proved to be the most suitable and is the most widely used for treatment process as it is relatively inexpensive, easy to produce and highly stable (Matsuoka & Masakazu, 2009).

Since Malaysia (located at 3.1 °N and 101.7 °E) is in the tropical region, it enjoys a conducive climate with abundance natural resource of sunlight. Sunlight has been proposed as having promising role in improving the water quality. However, solar treatment process is lengthy and its efficiency is very much affected by daily and diurnal change. Therefore, to increase the treatment efficiency and promote the practicality of using solar in treatment process, the use of the TiO_2 photocatalyst has been suggested in this study.

This paper describes how photocatalysis treatment could become a significant sector of the water treatment technologies for pesticide contaminated water. It evaluates the photocatalysis process that makes use of natural sunlight and UV radiation in a pilot plant with TiO_2 as the catalyst.

MATERIALS AND METHODS

Analytical Method

The total organic carbon measurement was performed using an on-line Total Organic Carbon analyser (Siever 900). Pesticides analyses were performed using Liquid Chromatography – Mass Selective-Mass Selective Detector (Applied Biosystems 3200Q Trap with Phenomenex Synergi 4u Fusion-RP 80A 50 x 2 mm). The mobile-phase composition was acetonitrile and water with 0.1 % formic acid and 5 mM ammonium formate.

Pilot Plant Design

Figure 1 shows a diagram of the integrated photocatalytic treatment plant that was used for the study. The pilot plant was constructed next to an underground well in a vegetable farming at Cameron Highlands where pesticide contamination was confirmed. The pilot plant was made up of the preliminary treatment system and the photocatalytic treatment system. The preliminary treatment system is used to remove coarse solids and other large materials often found in raw water. Removal of these materials is necessary to enhance the operation and maintenance of the subsequent treatment unit namely the photoreactor.

The photoreactor consists of five glass tubes with a total irradiated area of 0.53 m^2 connected in series and mounted on a fixed platform that can be tilted at 90°. The TiO_2 photocatalysts were packed into the glass tubes with 7400 $gTiO_2/m^2$. The TiO_2 photocatalyst used in this study was supplied by Photocatalyst Material Inc, Japan. Water flowed at 6.8 L/min directly from one tube to another tube. The photoreactor was operated in a recycle mode and the photoreactor is connected by a recirculation pipe with a 1 m^3 stainless steel tank. The water coming from the preliminary treatment was pumped into the tank with approximate volume of 250 litre. The photocatalytic treatment started when the water was pumped to the photoreactor. The water recycled between the tank and the photoreactor. The degradation and mineralization of pesticide were monitored as Total Organic Carbon (TOC). The solar UV intensity was measured using Kipp Zonen UV radiometer.

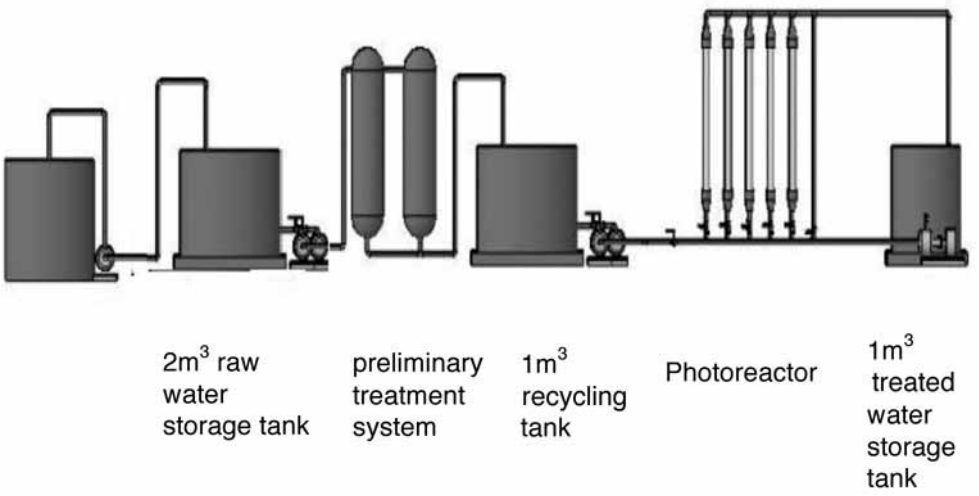

Figure 1. *A schematic diagram of the pilot plant.*

RESULTS AND DISCUSSION

Figure 2 shows the results of the photocatalytic reduction of TOC in the presence of solar and UV radiation. From the results, it is clear that solar and UV radiation are able to degrade the organic contaminants in the water. As the initial TOC concentration of the groundwater source was varied in which it depends on the farming activity of the day, no comparison can be done. However, in Figure 3, it is observed that after 14 hours of UV radiation, the degradation percentage of TOC was about 60 % and the degradation percentage of TOC is about 80 % after 24 hours of UV exposure. The degradation rate of 38 % is attained after 14 hours irradiation under sunlight exposure. However, only 54 % of degradation is observed under 24 hours solar radiation.

Figure 4 shows the total organic reduction by photocatalytic reaction as a function of accumulated solar energy in the presence of solar and UV radiation, respectively. The reaction rate is a sum of parameters which include several organic products inclusive of pesticides listed in Table 1. It is clear that the solar radiation requires high accumulated energy for mineralization of TOC. A smaller reduction of TOC of 47 % is observed under the solar radiation as compared to 74 % in the case of UV radiation by accumulating energy of 270 KJ/L which corresponds to 20 hours exposure as shown in Figure 3. This is a rather inefficient process in mineralization under solar radiation, although the process has an advantage of using natural sunlight as environmentally friendly technology. Further improvement is needed for practical applications of industrial and environmental interests.

Table 1 indicates the pesticide compounds that contribute to the TOC content. Results of Table 1 show that the pesticides are degraded under UV photocatalysis and solar photocatalysis. A few pesticide compounds such as aldicarb, methomyl, terbufos and thiphanate methyl are completely mineralized after 37 hours of UV exposure. Thiofanox sulfone and thiphanate methyl can be mineralized under 16 hours of solar illumination. Under these circumstances, it is demonstrated that photocatalytic treatment using TiO_2 as catalyst can mineralize pesticide residue in water. The complete mineralization of pesticides may require a prolong UV/ sunlight exposure which is dependent on the stoichiometry reactions of each pesticide compound.

The stoichiometry reactions of the pesticide compounds are as follows (Fernandez-Alba *et al.*, 2002; Malato *et al.*, 2001, 2003; Marinas *et al.*, 2001:

$C_7H_{14}N_2O_2S + 13.5O_2 \rightarrow 7CO_2 + 5H_2O + H_2SO_4 + 2HNO_3$ ……..aldicarb

$C_7H_{14}N_2O_4S + 12.5\ O_2 \rightarrow 7CO_2 + 5H_2O + H_2SO_4 + 2HNO_3$ …….aldicarb sulfone

$C_7H_{14}N_2O_3S + 13\ O_2 \rightarrow 7CO_2 + 5H_2O + H_2SO_4 + 2HNO_3$ ……..aldicarb sulfoxide

$C_5H_{10}O_2N_2S + 10.5O_2 \rightarrow 2HNO_3 + H_2SO_4 + 5CO_2 + 3H_2O$……....methomyl

$C_8H_{14}N_4OS + 17.5O_2 \rightarrow 8CO_2 + 5H_2O + H_2SO_4 + 4HNO_3$ …….metribuzin

$C_{10}H_{14}N_2 + 16O_2 \rightarrow 10CO_2 + 6H_2O + H_2SO_4 + 2HNO_3$ …… nicotine

$C_{10}H_{11}N_5O + 18.5O_2 \rightarrow 10CO_2 + 3H_2O + 5HNO_3$ …….. pymetrozin

$C_9H_{21}O_2PS_3 + 19O_2 \rightarrow 9CO_2 + 6H_2O + H_3PO_4 + 3H_2SO_4$ ……terbufos

$C_9H_{18}N_2O_4S + 15.5O_2 \rightarrow 9CO_2 + 7H_2O + 2HNO_3 + H_2SO_4$ …….. thiofanox sulfone

$C_{12}H_{14}N_4O_4S_2 + 21.5O_2 \rightarrow 12CO_2 + 3H_2O + 4HNO_3 + 2H_2SO_4$ ...thiphanate methyl

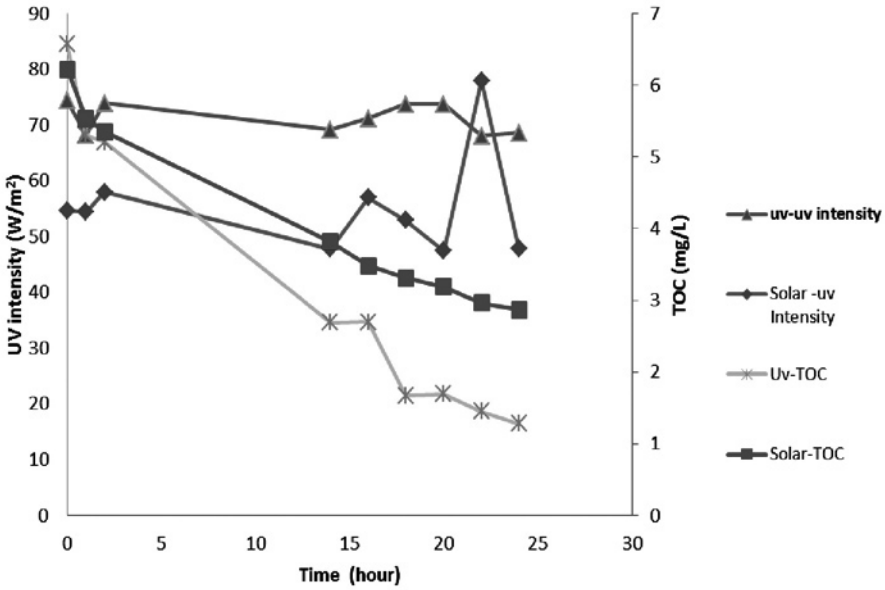

Figure 2. Total Organic Carbon reduction under solar and UV radiation

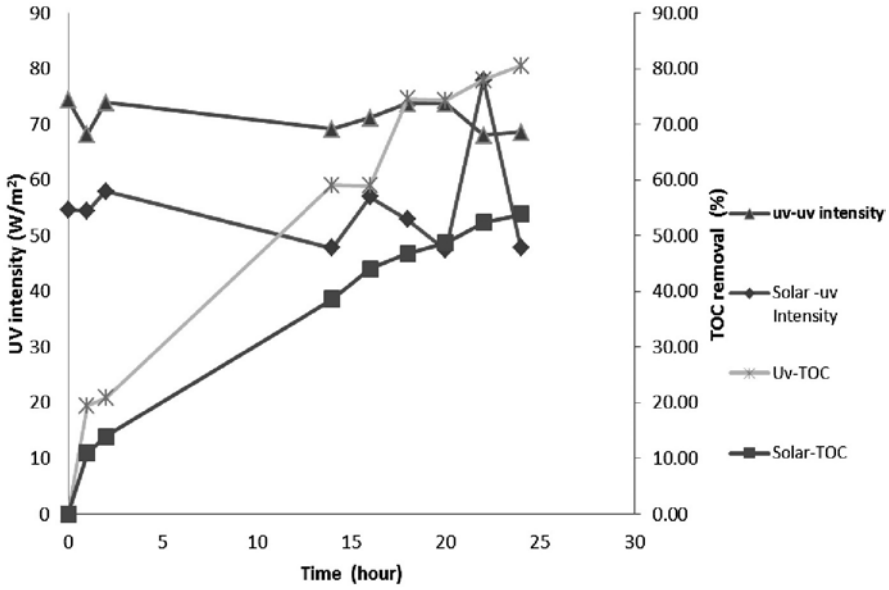

Figure 3. Total Organic Carbon removal efficiency under solar and UV radiation

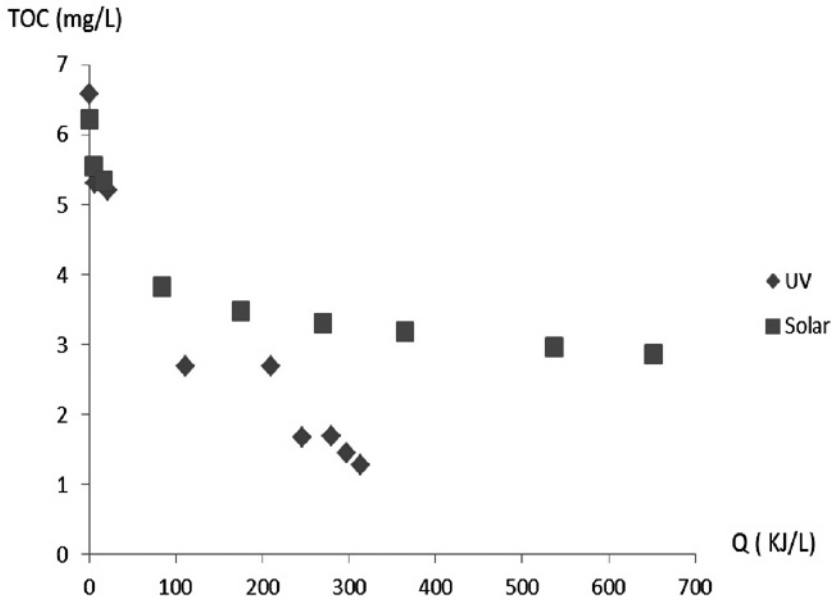

Figure 4. Total organic reduction by photocatalytic reaction as a function of accumulated solar energy in the presence of solar and UV radiation calculated according to Malato *et al.*, 2003.

Table 1. Results of pesticide concentration under photocatalytic treatments after 37 hours of UV radiation and 16 hours of solar radiation

Parameter	UV (µg/L)		solar (µg/L)	
	before	after 37 hours exposure	before	after 16 hours exposure
Aldicarb	0.0695	ND	0.663	0.162
Aldicarb Sulfone	0.813	0.462	ND	ND
Aldicarb Sulfoxide	11.5	2	2.56	0.138
Methomyl	0.103	ND	ND	ND
Metribuzin	0.457	0.0687	0.0608	0.0102
Nicotine	0.23	0.168	0.161	0.121
Pymetrozin	0.27	0.209	ND	ND
Terbufos	1.56	ND	0.925	0.69
Thiofanox Sulfone	125	0.924	52.8	ND
Thiphanate Methyl	0.112	ND	0.0287	ND

CONCLUSION

The detoxification of water containing pesticides had been demonstrated by photocatalytic treatment without total mineralization. The results showed that the photocatalytic treatment can mineralize the pesticide contaminants in groundwater.

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