EFFECT OF ADSORBENTS COATED WITH TITANIUM DIOXIDE ON THE PHOTOCATALYTIC DEGRADATION OF PROPOXUR

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ABSTRACT

Photocatalytic oxidation of pesticides in aqueous media irradiated by UV light is a rapidly growing field of research.   Therefore, the treatment technology for degradation of propoxur (an insecticide)   using titanium dioxide coated on the supports such as activated carbon, zeolite, brick, quartz and glass beads, was performed in this research.   Results show that GAC/TiO_2 is the best complexing agent for oxidizing propoxur because of its adsorption properities.   The others follow the sequence: plain TiO_2 > glass beads > zeolite > brick > quartz. The degradation rate of propoxur with plain TiO_2 is higher than that with TiO_2/GAC complexing agent.   But the mineralization rate of propoxur with plain TiO_2 is lower than that with TiO_2/GAC complexing agent. However, it can be concluded that using GAC as the support can improve the photocatalytic efficiency   ©1998 Elsevier Science Ltd. All rights reserved

KEY WORDS

Photocatalytic oxidation; supported titanium dioxide; propoxur; insecticide

INTRODUCTION

Most pesticides are non-selective; they are also harmful to ecological systems as well. Therefore, in addition to applying pesticides, the pollution prevention of pesticides used in our environment has to be considered. Photocatalytic oxidation is a promising technology in treating wastewater containing pesticides. Studies have shown that illumination of semiconductor powders in aqueous solutions

containing organic compounds and oxygen induces oxidative decomposition of organic compounds [1-5]. TiO_2 catalyzed the oxidation of organic pollutants in the presence of UV radiation at photon energies equal to or greater than the band-gap energy . The quantum efficiency of the process is influenced by electronic processes, reactor design, solution composition, the organic substrate, light intensity and surface interactions.

In the last few years, much attention has been devoted to the heterogeneous photocatalytic oxidation with fixed-bed reactors [3,6,7]. It is agreed that the critical step of organic compounds oxidized in the reaction is initiated with hydroxyl radicals produced on the photocatalyst surface [1-3]. Therefore, the adsorbability of the pollutants onto the photocatalyst surface is an important factor in evaluating the efficiency of the photocatalytic reaction. To promote the decomposition efficiency, it may load photocatalyst on suitable adsorbents to concentrate the pollutants on the photocatalyst surface. Matthews [8] suggested that the use of TiO_2 coated on sand permits economic scaling up of the process. Uchida et al., [9] demonstrated the photomineralization of propyzamine, a herbicide, with TiO_2 / activated carbon complexing agent in dilute aqueous solution. Kato et al., [10] also used the porous alumina ceramic as the supporter to study the photocatalytic property of TiO_2.

In our previous studies, photocatalytic oxidation of pesticides was investigated with TiO_2 coated on the inner surface of a glass tube. The photocatalytic oxidation of pesticides follows the Langmuir-Hinshelwood-type behavior, indicating that adsorption may play an important role in the oxidation reaction [3-5]. However, it was noted that wherever the reaction occurs, at the surface or in the bulk, the rate reactions have the same analytical form as the Langmuir-Hinshelwood expression [11]. Therefore, this research is to study the photocatalytic process with titanium dioxide coated on supports, such as activated carbon, zeolite, brick, quartz and glass beads to investigate the characteristics of the photocatalytic reaction. Propoxur, an insecticide, was used as a test chemical.

MATERIAL AND METHODS

Propoxur was obtained from Bayer Company with purity of 96.3%. The photocatalyst, TiO_2 , used in this study was Degussa P25, 50 m^2/g, 30 nm mean particle size obtained from the Degussa Company (Germany). The supports, activated carbon, zeolite, brick, quartz and glass beads, were obtained from the San-Yu Company (Taiwan). The water used for experiments was purified by a Milli-Q/RO system (Millipore) and has a resistivity greater than 18 $M\Omega/cm$. All other chemicals used are of reagent grade without further purification.

The supports were coated with TiO_2 by preparing a TiO_2 suspension in 100 ml water (sonicated for a few minutes), adding supports to the sonicated suspension and evaporating to dryness in an oven at 100 ^0C. The amounts of TiO_2 and supports added in this procedure depended on the experimental conditions. The coated supports were then heated at 550 ^0C for half an hour to produce the complexing agents.

The photocatalytic reactor is shown in Fig. 1. The reaction was conducted in a 1.2-liter double-jacked vessel with a quartz cover; the volume of reaction mixture was 1 liter. Quartz cover was required for the shorter wavelength of UV light. The cut-off wavelengths for quartz are less than 200 nm. Therefore, 254 nm light can pass through the cover to excite the TiO_2. The UV radiator was composed by three 10 w low pressure mercury lamps with a major emission at 254 nm (Sankyo Ltd., Japan) and was located above the reactor.
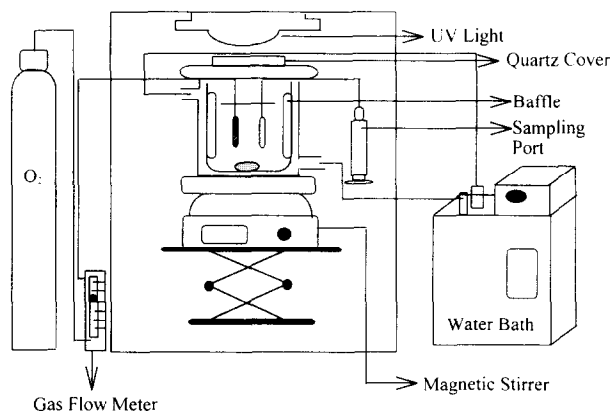

Fig. 1. Photocatalytic reactor used in this study

For all experimental runs performed in this study, the pH of the reacting mixture was adjusted initially. During experiments, the reactant solution was agitated continuously with a magnetic stirrer and oxygen (99.9 % purity) was bubbled into the solutions at a constant flow of 50 ml/min to insure oxygen saturation. The samples were taken from the solution with certain time intervals. Propoxur was analyzed with a HPLC (Waters LC module 1), total organic carbon (TOC) was detected with a TOC analyzer (ASTRO Model 2001), and surface area was determined with a ASAP 2000 BET analyzer.

Potassium ferrioxalate solution was used to measure the photon flux in the reactor. The quantum yield (QY) can be defined as the ratio of the number of molecules reacting to that the photons supplied. Based on reaction with TiO_2 - free actinometry solutions for the reactor, the flux rate was 7.2×10^{-4} M/min if the quantum yield for ferrous ion formation in the ferrioxalate solution is taken to be 1.28 [12].

RESULTS AND DISCUSSION

Photocatalytic degradation of propoxur with different complexing agents

Choosing a proper support with a better ability of adsorption can improve the photocatalytic efficiency since the support can concentrate organic chemicals on its surface.   Since 3g complexing agent with 0.15 g TiO_2 coated were immersed in aqueous solutions to start the photocatalytic reaction, 0.15 g plain TiO_2 was also dispersed in the reaction solution.

Table 1.   Surface areas of coated and uncoated supports

Support and Complexing agent*	Surface Area (m^2/g)
Plain TiO_2	50
GAC	902
Coated GAC	745
Quartz	4.90
Coated Quartz	4.57
Zeolite	8.90
Coated Zeolite	4.95
Glass Beads	5.70
Coated Glass Beads	2.95

*: 1 g support was coated with 0.05g of TiO_2

Table 1 lists the surface areas of supports coated and uncoated TiO_2. The coating process eliminated the surface areas of complexing agent. The extent of surface area reduction depended on the characteristics of supports. As shown in Fig.2, GAC/ TiO_2 is the best complexing agent for propoxur removal. By comparing the surface areas among the complexing agents, it is obvious that surface area is not the only factor affecting on the propoxur removal. The complexing agent of glass beads has a low surface area, but the propoxur removal with glass/ TiO_2 is high than that with other complexing agents except GAC/ TiO_2. Clearly, except GAC, the supports coated with TiO_2 did not improve the efficiency of propoxur disappearance in this reaction system. The reason is that the illumination area was reduced when TiO_2 was coated on the support surface and the supports can not adsorb propoxur efficiently. However, since this study is   to find the proper support for improving the efficiency of propoxur removal. The large surface area of GAC induces not only propoxur but also TiO_2 adsorbs on GAC.   In fact, TiO_2 is a fine

particle that can disperse in the bulk solution, but if coated on the supporter surface, will result in a low efficiency of quantum yield because of surface area reduction. Based on the the experimental resulted mentioned above, the GAC is still worthy investigating in more details. Thus, in the following experiments, GAC was chosen as the medium.
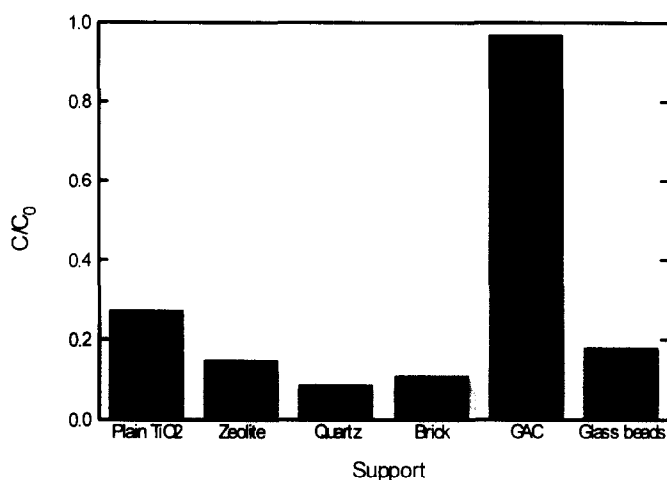

Fig.2   Propoxur removal after 60 min illumination with different complexing agents

Experimental conditions: [propoxur]=4.78x10^{-4} M; pH$_0$=4;

complexing agent, 3g

Effect of support diameter

To evaluate the effect of support size on propoxur oxidized, several diameters of GAC were used in this study.   Fig. 3 shows the time course of propoxur removal in the photocatalytic reaction over various diameters of GAC/ TiO$_2$ complexing agents.   The smaller GAC/ TiO$_2$ diameter, the faster propoxur disappearance.   However, it is difficult to separate the amount of propoxur adsorbed and oxidized on the GAC/ TiO$_2$ surface because the disappearance of propoxur is attributed to oxidation and adsorption in the same time.   Therefore, we compared the propoxur remainings in the GAC/ TiO$_2$ solutions with and without UV illumination to find the effect of GAC diameter on the disappearance of propoxur.   Table 2 indicates the influence of GAC diameter on the disappearance of propoxur with and without UV illumination.

In general, the rate of propoxur disappearance with UV illumination is slightly higher than that without UV illumination because GAC is an excellent adsorbent resulting in a higher adsorption rate than oxidation rate. Thus, UV light can not make a significant effect on the propoxur removal in the GAC/ TiO$_2$ solutions. However, according to Table 2, it is proved that oxidation reaction really happened , and its rate was much lower than that of adsorption.
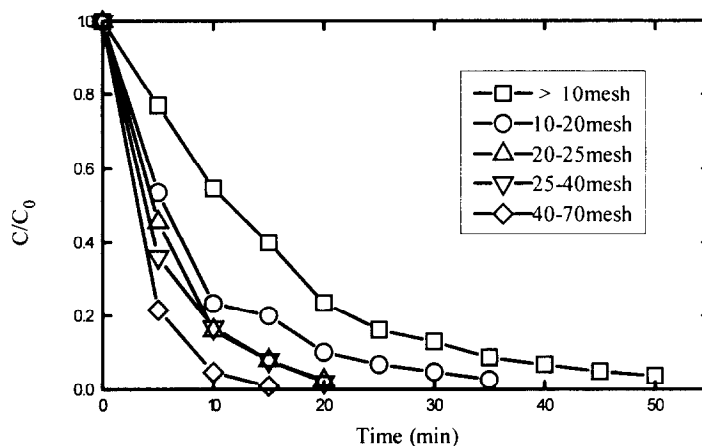

Fig.3   Effect of GAC diameter on the photocatalytic oxidation of propoxur

Experimental conditions: [propoxur]=4.78x10^{-4} M; pH$_0$=4;

complexing agent, 3g

Table 2   Effect of   GAC diameter on the adosrption and oxidation of propoxur*

Diameter		Propoxur remaining(%)	
mesh	mm	without illumination	with illumination
70~40	0.21~0.42	2.5	1.2
40~25	0.42~0.707	8.6	8.1
25~20	0.707~0.841	11.5	8.3
20~10	0.841~2	31	20
>10	>2	39.9	40

*Propoxur remainings are compared at 15 min of reaction time.

Effect of TiO₂ loading

TiO₂ loading is another important factor for propoxur oxidation. With plain TiO_2, the photocatalytic rate increases with increasing the TiO_2 loading . However, the rate will be reduced because UV light is blocked by catalyst itself. In this experiment, four kinds of TiO_2/GAC were prepared; 0.05g, 0.1g, 0.15g, 0.2g and 0.25g TiO_2 were coated on 1g GAC, separately. Fig.4 indicates the effect of TiO_2 loading on the photocatalytic oxidation of propoxur. Increasing the amount of TiO_2 coated on the GAC surface induces the increase of oxidation rate. However, the results shows that the oxidation rate with 0.15 and 0.2 g TiO_2 can almost perform as well as that with 0.25 g TiO_2 . The present instance is assumed to be the reason that the illumination area do not increase due to a higher catalyst concentration.
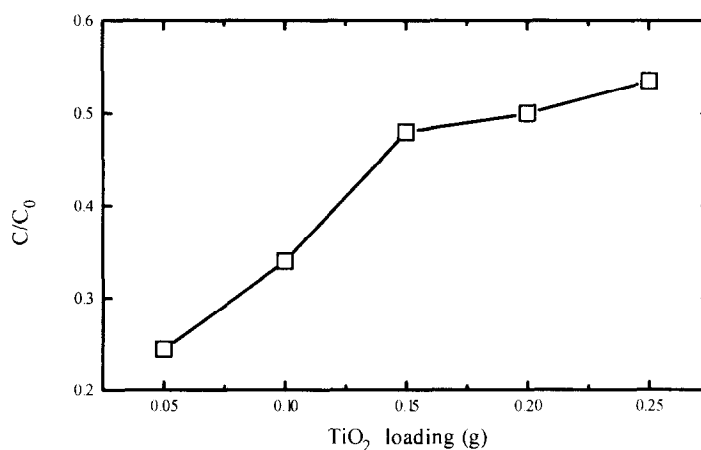

Fig. 4   Effect of TiO_2 loading on the photocatalytic oxidation of propoxur
Experimental conditions: [propoxur]=4.78×10^{-4} M; pH_0=4;
complexing agent, 1g; illumination time, 5 hr

Oxidation and adsorption of propoxur on the TiO₂/GAC surface

As GAC is an excellent adsorbent, therefore, the disappearance of propoxur in the solution resulted from the adsorption and oxidation reaction; propoxur and its oxidation intermediates were concentrated on the complexing agent surface and then oxidized. According to this characteristics of the complexing agent,

it was found that the disappearance of propoxur from the aqueous phase was mainly attributed to adsorption. In this experiment, the oxidation rate on the complexing agent surface can not be measured and then we hardly distinguished the amount of propoxur oxidized and adsorbed in the combined reaction. For this reason, the adsorption of propoxur on the complexing agent surface was furthur studied.

Fig.5 shows the propoxur remaining during the adsorption reaction. It was found that the amount of propoxur adsorbed on the surface of complexing agent reached a saturation after 3 hours. Therefore, the photodegradation experiment described below were carried out with a preadsorption of propoxur on the complexing agent for three hours. It is assumed that the disappearance of propoxur from the aqueous phase is attributed to oxidation with a preadsorption process because the rate of adsorption is much higher than that of oxidation. Fig.5 also shows the photocatalytic oxidation of propoxur with a preadsorption process. The reduced amount of propoxur from the aqueous phase is assumed to be resulted from the oxidation reaction.
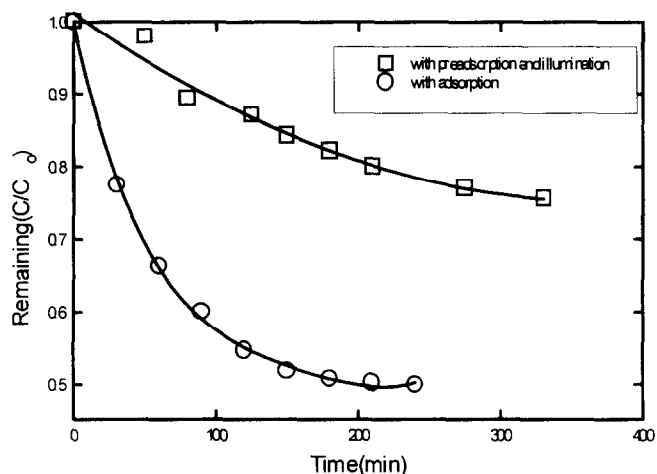

Fig.5 Adsorption and photocatalytic oxidation of propoxur
Experimental conditions: [propoxur]=8.6×10^{-4} M; pH_0=4;
complexing agent, 1g

Comparison of photocatalytic reactions onto the surfaces of plain TiO_2 and TiO_2/GAC

To compare the catalytic activity of plain TiO_2 and TiO_2/GAC, 0.25 g TiO_2 was used for coating on 1g GAC and dispersing directly in the solution, respectively. In the TiO_2/GAC system, 1 g complexing

agent was immersed in a solution containing 9.56×10^{-4}M propoxur to proceed the preadsorption reaction for saturating the complexing agent surface. After three hours, the UV light was turned on to initiate the photocatalytic reaction. The initial concentration of propoxur was 4.78×10^{-4}M. In the plain TiO_2 solution, the initial propoxur solution was also 4.78×10^{-4}M. In these two reaction systems, propoxur oxidation followed a first-order kinetic behavior. Table 3 lists the kinetic data of propoxur oxidation. The oxidation rate of propoxur with plain TiO_2 is slightly higher than that with TiO_2/GAC complexing agent. But the mineralization rate of propoxur with plain TiO_2 is somewhat lower than that with TiO_2/GAC complexing agent.

Table 3   Rate constants of propoxur oxidation

Catalyst	Rate constant(1/hr)	
	Mineralization	Oxidation
TiO_2/GAC	0.024	0.096
TiO_2	0.018	0.102

Without preadsorption process, propoxur removal rate in the solution containing TiO_2/GAC was much higher than that containing plain the TiO_2 because GAC is an excellent adsorbent that can adsorb propoxur on its surface in a short period of time. From the HPLC analysis, there were less intermediates found in the TiO_2/GAC system. It is assumed that the intermediates formed in this system were adsorbed onto the surface of complexing agent. In the plain TiO_2 system, the intermediates produced in the reaction remained in the aqueous phase that can be detected by TOC analysis. Trimoto et al.[12] have also reported that the use of adsorbent supports can ehhance the rate of mineralization of propyzamide and reduce the concentration of solution-phase intermediates. In this study, the supply of the adsorbed propoxur to the GAC/ TiO_2 interface occurs very fast as compared with the collision of dissolved propoxur of a dilute concentration to the suspended TiO_2 surfaces. The use of plain TiO_2 allows the dissolution of intermediates into solution due to low the adsorbability, and dissolved propoxur and intermediates are oxidized further to give a variety of other intermediates when they collide with TiO_2. In conclusion, the complexing agent has a large capability of collection of degradation intermediates as well as the target substrate from the solution phase onto the complexing agent. The photons entering the reactor with plain TiO_2 can be almost absorbed by the photocatalyst as TiO_2 dispersed completely in the reactor. TiO_2 supported on the GAC can not ultilize all the photons entering the reactor to produce radicals for degrading propoxur and intermediates because TiO_2 is concentrated on the surface of 1 g

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GAC . However. the oxidation efficiency with GAC/ TiO_2 is almost as that with plain TiO_2 even the GAC/ TiO_2 system utlized less amount of photons. Therefore, it can be concluded that using GAC as the support can improve the photocatalytic efficiency and it is necessary to optimum light utlization for GAC/ TiO_2 system.

CONCLUSIONS

The rates of photocatalytic oxidation of propoxur have been determined in the presence of TiO_2 coated supports. TiO_2/GAC is the best complexing agent for oxidizing propoxur because of its adsorption properties. The others follow the sequence: aked TiO_2 > glass beads > zeolite > brick > quartz. The degradation rate of propoxur with plain TiO_2 is higher than that with TiO_2 /GAC complexing agent. However, the mineralization rate of propoxur with suspended TiO_2 is lower than that with TiO_2/GAC complexing agent. The catalyst coated on the blunt supports eliminates the problem of filtration associated with the use of catalyst suspensions but the reaction rate is mass transfer limited. The use of TiO_2 coated on the GAC permits the promotion of the decomposition efficiency for the pollutants. The chief loss of quantum efficiency in TiO_2 /GAC system is due to the small illumination area comparing with plain TiO_2 . Therefore, the reactor design to permit optimum light adsorbed by TiO_2 /GAC is necessary.

ACKNOWLEDGMENT

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