

Visible Light Driven Photocatalyst for Degradation of Organophosphate Pesticides: A Review

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Abstract: Organophosphates (OPs) are insecticide used to replace the persistence organochlorines (OCs). OPs are the effective insecticide used to control pests to enhance crops productions. Due to the strong recalcitrant properties, OPs cannot totally be degraded by conventional wastewater treatment process and the effluent causes negative impacts to the environment. The effectiveness of the AOPs is relied on the strong radical namely hydroxyl radicals ($\bullet\text{OH}$) which can convert the pollutants into less harmful products. Photocatalysis is one of the AOPs widely practiced in water treatment process. A good photocatalyst must able to promote the electron from its valance band to the conduction band and the prevent the photogenerated electrons from returning to its valance band. The electron generated was further reacted with oxygen to form peroxy radicals, $\bullet\text{O}_2^-$. The hole (h^+) formed was then react with water molecule to form $\bullet\text{OH}$. Titanium dioxide, TiO_2 is well known photocatalyst which only can be activated under ultra-violet light. Visible light photocatalysts are in the current research trend as they are found to be an effective method to degrade contaminants in wastewater. Various type of dopants has been doped on the TiO_2 with different method purposely to shift the absorption of light from the UV light region to visible light region. The purpose of this review is to present the studies on different preparation method of the modified TiO_2 and application of the modified TiO_2 in degrading different types of OP pesticides. Finally, the need for present and further research on OPs wastewater also briefly discussed.

Keywords: Visible light photocatalysis, organophosphate, recalcitrant, pesticide wastewater, degradation

INTRODUCTION

Organophosphates (OP) are artificial pesticides found during the Second World War to replace the organochlorine pesticides [1] because they are not biodegradable by microorganisms as it is a strong class of carcinogenic water/wastewater contaminant [2]. Photocatalytic is well known as low cost, environmentally friendly and sustainable water treatment technology to remove different classes of the poisonous organic pollutants under various type light irradiation [3,4].

1.0 Need for removal from environment

Adverse effects of the pesticides that appeared in water and food have brought the great concern of scientific community [5]. Human health would be affected by the low concentration of pesticide residue (at $\mu\text{g/L}$ or ng/L) in the water such as neurodevelopment diseases, weakening of the immune system, cytotoxicity and mutagenicity. Besides that, endocrine system of

mammals are also affected when the poisonous pesticides enter the body [6,7,8,9].

1.1 Conventional pesticide wastewater removal techniques

Wastewater treatment method was first developed to deal to the adverse conditions caused by the discharge of wastewater to the environment and care for the public health [10]. From the early 1900 to 1970s, wastewater treatment focus on the BOD, suspended solids, pathogenic microorganism. After that, the objectives of the treatment expanded due to the awareness towards the water pollution and its long term effects to human health [10]. Several wastewater treatments, such as physical, chemical and biological process involving absorption, oxidation, catalytic degradation, membrane filtration and biological treatment have been performed [10,11,12,13]. Physical treatment does not completely mineralize the pollutants as it only transform them from one form to another form [15]. Meanwhile, chemical oxidation is costly and decontaminates the water with the toxic pollutants used [16]. Only a few specific fungal and

bacteria were capable to be used as microbial degradation of pesticides [17] but the degradation process required a long period of time. Advantages and weakness of different water treatment are listed in Table 1.

Table 1: Advantages and weakness of the wastewater treatments process

	Advantages	Weakness	Ref.
Conventional			
Biological activated carbon	Residual disinfection or oxidation products can be removed	Sludge is generated and hard to dispose	[18]
Activated sludge	Low operation costs compared to AOPs	Cannot be used in treatment when COD levels are more than 4000 mg/L.	[19]
Chemical process			
Coagulation	Reduced the turbidity of water and increased the rate of sedimentation	Large amount of sludge is produced and micropollutant cannot be removed.	[19]
Physical process			
Membrane filtration	Useful in treating wastewater influents, Applicable in heavy metal, dye and pesticide removal.	High energy requirement, membrane fouling	[19,20]

2.0 Photocatalyst

Photocatalyst, one of the advanced oxidation processes has been proven as an advanced and convenient way to mineralize toxic organics into harmless substances without the aids of extra chemicals in order to prevent the sludge production and its disposal [21]. Recently, many researchers have switched the studies from UV light-driven photocatalyst to visible light catalyst because there is only less than 5% of UV in the solar spectrum [22] while visible light occupied for 45% in the solar spectrum [23]. Thus, visible light driven photocatalysts can be used to degrade the organophosphates pesticides and more studies ought to

be done in order to achieve greater results in degrading recalcitrant pesticides wastewater in Malaysia pesticides manufacturing industries in order to meet the effluent standard set up by Environmental Quality Act (EQA) 1974 as shown in Table 2. Therefore, more efforts should be done in this field in order to achieve efficient results which can be employed in industrial sectors. This mini review is written to address the common methods used to prepare modified TiO₂ and the results of the certain OPs (methyl parathion, malathion and diazinon) removal using visible -light driven TiO₂ photocatalyst.

Table 2: EQA regulation for discharge of treated wastewater

Parameter	Effluent Discharge to Rivers/ Stream				Effluent discharge to Stagnant Water Bodies			
	Standard A		Standard B		Standard A		Standard B	
	Absolute	Design	Absolute	Design	Absolute	Design	Absolute	Design
BOD	20	10	50	20	20	10	50	20
SS	50	20	100	40	50	20	100	40
COD	120	60	200	100	120	60	200	100
AMN	10	5	20	10	5	2	5	2
Nitrate	20	10	50	20	10	5	10	5
Nitrogen Total	N/A	N/A	N/A	N/A	5	2	10	5
Phosphorus O&G	5	2	10	5	5	2	10	5

2.1 TiO₂

Titanium is an inactive chemical element which is the ninth most common element found in the earth's crust. Its straightness is comparable with steel but its weighs 45% less than steel [24]. It appears as white solid with high thermal stability, inflammable, low solubility in water and strong anticorrosion [25]. TiO₂ is made up of different rocks and minerals, thus, different types of TiO₂ is formed such as rutile, anatase, brookite and Titanium dioxide (B) [25]. Differences in crystal structures and bandgaps of each type of titanium is shown in Table 3.

Table 3: Bandgap and crystal structure of different phase of TiO₂

Phase	Band Gap (eV)	Crystal Structure
Anatase	3.2	Tetragonal
Rutile	3.0	Tetragonal

[26]

2.2 Preparation of modified TiO₂

The photodegradation performance of TiO₂ is relied on following factors: (a) light absorption properties (b) the rate of separations of electrons and holes pairs and (c) the rate of recombination of electrons and holes [27].

The wide band gap of TiO₂ restricts its light absorption in visible light region [28]. TiO₂ itself can be classified into different types such as Degussa P25, Millennium PC50, PC100, PC105, PC500 UV100 and TTIP (titanium tetraisopropoxide) [29]. Dopants poses excellent physiochemical properties such as formation of crystal with small size with high specific surface area [30]. Two types of dopants normally used, namely metals such as silver (Ag) [31], Palladium (Pd), Gold (Au) [32] and non - metals such as nitrogen (N) [33] and carbon (C) [34] There are 2 common methods to prepare the modified TiO₂ namely (1) sol gel method (2) impregnation – precipitation-photoreduction.

2.1.1 Sol-gel method

Sol-gel has been practiced since mid-1800s. This method is used to prepare thin film and powder catalyst [35]. Tetrabutyl titanate (Ti(OBu)₄) [36] [37] and titanium tetraisopropoxide, TTIP [38] are two common TiO₂ in liquid form used in sol-gel method. During the process, alcohol is added as the boiling point of alcohol controlled the particle size [39]. Acidifying agent is added to produce larger size of TiO₂ [40] and study showed that hydrochloric acid (HCl) able to form anatase even the temperature was low [41]. High calcination temperature is required for this reaction (100 -450 °C) [42][38]. Although many reviews showed that sol-gel method can produce photocatalyst with high efficiency, the production cost is expensive as TTIP and Ti(OBu)₄ are expensive than powdered TiO₂. Meanwhile The high calcination temperature consumed massive amount of electricity. Besides, the dopants were normally doped by another method such as impregnation - precipitation – photoreduction. Table showed the TiO₂ which are prepared by sol gel method and their application in water treatments.

Table 4: Sol sel method prepared photocatalyst and their application in wastewater treatments.

Photocatalyst	Contaminant	Results	Ref.
Ag/AgBr/TiO ₂	Ibuprofen and <i>E. coli</i>	The sol gel prepared TiO ₂ had stronger antibacterial activities in the dark compared to previous reviews.	[38]
TiO ₂ / fly ash cenospheres (FAC)	rhodamine B	TiO ₂ /FAC could not degrade rhodamine B compared with Ag/AgBr/TiO ₂ /FAC prepared with two-step approach.	[43]

2.1.2 Impregnation - precipitation -photoreduction

Impregnation defined as the fine distribution of chemicals and/or metal particles in the pore of certain reactants [44]. Some of the visible light-driven-photocatalyst (metal /metal halide) were prepared with this method [41,42,43]. Powdered TiO₂ normally used in this process. During the process, powdered TiO₂ was impregnated with the dopants (in aqueous form) and stirred for certain time. The solution was then precipitated with metal halide and then irradiated with light before dried it in the oven. Meanwhile photoreduction is used to deposit the noble metal particles on a semiconductor using light irradiation [48]. This method is simple as the preparation time is shorter than other methods. In addition, High calcination temperature is not required for this process. Thus, it can be prepared easily in the laboratory.

Photocatalyst	Contaminant	Ref.
Ag/AgCl/TiO ₂	Dye (Methyl orange)	[49]
Ag/AgCl/TiO ₂	Dye (Brilliant red)	[50]

3.0 Organophosphate pesticide wastewater

Wastewater containing organophosphate cannot totally removed by biological techniques [51]. The United States Environmental Protection Agency (USEPA) set up the wastewater constituents from pesticides manufacturing and formulation plants as summarized in Table 5. In Malaysia, very few studies have been done on the pesticide and the information is still lacking [52]. Based on the studies, pesticide residues had been detected in Perak, Selangor and Penang and also the sediments in Sabah and Sarawak [53].

Table 5: Summary of raw wastewater constituents

Pollutant group	Design level (mg/L)	Ref.
Volatile aromatics	127–293,000	[54]
Halomethanes	122–2600	
Cyanides	5503	
Phenols	100–42,000	
Copper	4500	
Zinc	247	
Pesticides	10–11,200	
BOD	0–60,000	
COD	14–1,220,000	
TTS	2–4090	

3.1 Methyl parathion (O,O-Dimethyl-O-p-nitrophenyl- phosphorothioate)

EPA has classified the methyl parathion (MP) as class I toxicity [55]. Overexposure to methyl parathion could lead to chronic diseases such as modulating reproductive, carcinogenic and immunosuppressive effects [56]. Methyl paraoxon, the main oxidation product of methyl parathion showed greater toxicological effect than its parent compound [57]. Visible light photocatalytic degradation of methyl parathion with various concentrations from 50 µg/L to 250 µg/L was conducted by mixing it with nitrogen (N) doped TiO₂ from triethylamine precursor photocatalyst under 125 W visible tungsten halogen lamp that emits wavelengths ranging from 340 to 860 nm. The result revealed that complete degradation of 50, 100 and 250 µg/L of methyl parathion consumed 75, 105 and 135 min for a suspended form of N-doped TiO₂ whereas 60, 90 and 120 min was required for immobilized N-doped TiO₂ to degrade the same concentrations of methyl parathion [58]. Another experiment conducted where Fe₃O₄@SiO₂@TiO₂ able to totally remove 100 mg/L of MP under UV irradiation [59]. Compared with biological treatment method, an experiment was conducted where cyanobacterial strain was used to remove MP with the process known as biosorption where

the cyanobacterial strain gained the phosphate from the MP. It consumed long time to incubate the cyanobacterial and the incubation was affected by the presence of light. The incubation of cyanobacterial only carried out in the light condition [60]. It is not suitable for huge MP manufacturing industries as the rate of bacterial incubation is lower than the rate of wastewater production. Visible- light driven photocatalyst shows its advantages as it can capture light whether it is UV light or visible light to start the photocatalytic activity.

3.2 Diazinon (O,O-diethyl O-[6 methyl-2-(1-methylethyl)-4-pyrimidinyl] phosphorothioate)

Diazinon is classified as class II which is moderately hazardous by World Health Organization (WHO) [61]. Diazinon concentration in the range of 90-444 mg/kg leads human to die, thus it is important to remove the residues from the water[21]. Experiment has been done to study the absorption efficiency of activated carbon (AC) and TiO₂. 0.03 g of the AC and TiO₂ were added separately with 40 mg/L diazinon and put in the dark for 80 min. It was found the absorption efficiency of AC was better than TiO₂. Another experiment was conducted to compare the photocatalytic of AC and TiO₂. It was found that the diazinon removal by AC-TiO₂ composite was better than TiO₂ alone under UV irradiation [21]. Another research conducted where xenon lamp with the wavelength in the range of 380–900 nm was used as light irradiator to degrade diazinon with different concentration. The result showed that 88% of 5.1 mg/L of diazinon was removed and mineralization percentage of 67.8% with 2.7 g/L of nitrogen- doped TiO₂ catalyst in pH medium of 5.9 while the removal efficiency was only 8% by photolysis and 18% by adsorption [62]. Degradation of 10 ppm diazinon was carried out by 0.1 Fe₂O₃/TiO₂ (metal dopant) The result showed the high removal as well [63]. It is found that absorption is a long-time consumption and low efficiency process. Expose to UV for long period can lead to skin cancer, visible light driven photocatalyst (produced with metal and non – metal dopant) can degrade diazinon as good as UV light. Table 6 showed the results for the absorption and visible light photocatalyst of diazinon wastewater.

Table 6: Different diazinon removal methods

Method	Initial concentration	Removal (%)	Time take (min)	Ref.
Absorption				
AC	40 mg/L	35	80	[21]
TiO ₂	40 mg/L	15	80	
Visible light photocatalysis				
TiO ₂ /Fe ₂	10 ppm	89.21	45	
O ₃ nanocomposite				[63]
N- doped TiO ₂	5.1 mg/L	88	88	[62]

3.3 Malathion (S-1,2-bis(ethoxycarbonyl)ethyl 0,0-dimethyl-phosphorodithioate)

Malathion is water soluble pesticides that could endanger to wildlife and public health [64]. Since it has high toxicity, the US EPA restricted the presentation of malathion in drinking water should not be higher than 0.1- 0.2 mg/L, thus its amount should be controlled in the water resources [65]. Au–Pd–TiO₂ visible light generated photocatalyst was used to study the photodegradation of malathion under irradiation of 450W high-pressure mercury lamp which emits the wavelength at 365 nm. The degradation rate yielded 98.2 % in 2 hours which is higher than bare TiO₂ which removed 73.8 % of malathion [66]. 1g/dm³ of N-doped TiO₂ photocatalyst was applied to degrade 100 mL of 15 ppm malathion and it was discovered that 97 % of malathion degraded within 150 minutes in pH medium of 6 under UV light with the wavelength of 364 nm which is fall in the visible light region. Meanwhile, the carbon oxygen demand (COD) was deduced from 50 to 10 mg implied that 80 % mineralization of the malathion [27]. The degradation of 12 mg/L of malathion with 1 g/L of 2 % WO₃/TiO₂ in pH medium of 7 and the result stated that degradation was completed in 120 min and 63% of the pesticide was mineralized after 300 minutes. Even though the experiments were carried out under natural solar irradiation, photocatalytic process absorbed visible light to start the reaction [68]. Hereby it can be justified that the presence of metals and non - metals dopant showed their ability to degrade the malathion without the chemical or materials that are required in other wastewater treatment process as shown in Table 7.

Table 7: Different malathion removal methods

Chemicals / Material required	Disadvantage	Ref.
Nanofiltration		
<ul style="list-style-type: none"> Membrane filter High pressure pump 	High energy consumption	
	Appropriate pore size and material must be known to produce a good membrane	[69]
Photo-Fenton reaction		
<ul style="list-style-type: none"> Hydrogen peroxide (H₂O₂) ferrous sulfate heptahydrate (FeSO₄·7H₂O) 	H ₂ O ₂ is needed to promote its effectiveness	

CONCLUSION

Photocatalysts have been proven as low cost and environmentally friendly technology in wastewater remediation process. However, most of the photocatalysts only can be activated by UV light. Although visible light driven photocatalysts have been used in degradation of organic pollutants such as dye water, pharmaceutical products and pathogenic microorganics, information on degradation of organophosphate pesticides by the visible light photocatalyst is still lacking. Some of the intermediates formed (oxons) during photolysis were more toxic compared to parent compounds. However, not many researches have conducted on the degradation of the by-products. Thus, monitoring the toxicity during the degradation is essential to ensure safer handling of pesticide wastewater. Form the review, we can conclude that visible light driven photocatalysts are able to accelerate the mineralization and degradation of the organophosphate pesticide was accomplished by the modified TiO₂. From the review, points on the future scope were summarized:

1. More study is needed to discover various types of visible light driven catalyst for degradation of OPs.
2. Rebuild the new tech wastewater treatment process can be burdening. We can combine the current biological treatment with photocatalysis in pre and post wastewater treatment. Thus, the sludge formation can be reduced and enhance the quality of water effluent in order to meet the EQA standard.

3 Most of the photodegradation of the pesticide experiments conducted in lab scale can be improved hence applicable in pesticide manufacturing industries.

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