

Impact of TiO₂ in Photolytic degradation of Pesticides in Wastewater

Priyanka Gupta¹ and Gaurav Tamrakar²

PhD Research Scholar, Department of Applied Chemistry¹

Shri Shankaracharya Technical Campus, Junwani, Bhilai, CG

Assistant Professor, Department of Mechanical Engineering, Kalinga University, Naya Raipur, CG²

priyanka.84may@gmail.com, gaurav.tamrakar@kalingauniversity.ac.in

Abstract: Removal by adsorption and photolytic degradation of organic pollutants from water are cost effective methods. But oxidation technologies are gaining interest as an effective approach for wastewater treatment capable of degrading a diverse spectrum of organic contaminants. The present-day assessment targets to focus on recent advancements in photocatalytic degradation of insecticides and main organic pollution. Photocatalysis is a promising advanced oxidation generation to relieve water pollutants troubles. Titanium dioxide (TiO₂) is the most popular photocatalyst due to its low price, nontoxicity, excessive oxidizing skills, and clean immobilization on various surfaces. The usage of TiO₂-based photocatalysts indeed, most of the strategies, which hired robust catalysts, confirmed and exhibited successful degradation of the pesticides beneath various situations. We agree with this topic of research is extremely crucial and could keep growing in current years, achieving final suitable outcomes and locate extra applications in special fields of take a look at.

Keywords: Photocatalysis; Pesticides; Water Treatment; Titanium Dioxide

I. INTRODUCTION

Photo catalytic degradation has been proved to be a promising approach for the remedy of wastewater contaminated with organic and inorganic pollutants. The procedure, as a means of elimination of persistent water contaminants along with pesticides, which exhibit chemical balance and resistance to biodegradation, has attracted the eye of many researchers in recent years (Bahnmann et.al 1994; Herrmann et.al 1999). Many of those investigations have utilized aqueous suspension of semiconductors illuminated by means of UV mild to photo degrade the pollution. The approach offers many advantages over conventional wastewater remedy strategies such as activated carbon adsorption, chemical oxidation, biological treatment, and many others. As an instance, activated carbon adsorption includes segment switch of pollution without decomposition and for that reason induces every other pollution hassle. Chemical oxidation is unable to mineralize all natural materials and is simplest economically suitable for the elimination of pollution at high concentrations. For biological treatment, the principle drawbacks are: sluggish response rate, disposal of sludge and the want for strict control of right pH and temperature. On this context, photo catalytic methods is very effective for the elimination of pollutants of low concentration from water (Konstantinou et.al. 2003).

Complete oxidation of organic pollutants within few hours. No formation of polycyclised products. Numerous catalysts had been studied as ability photo catalysts for this purpose. those consist of: ZnS (Yin et.al 2001), α-Fe₂O₃, g-Fe₂O₃ (Leland et. al. 1987), ZnO (Yesodharan et. al. 1980), TiO₂ (Sclafani et. al. 1990) ZrO₂, lanthanide tantallates. A number of the semiconductors used, TiO₂ is one of the most famous and promising materials, because of its stability underneath harsh situations, different allotropic forms with excessive photo activity, opportunity of coating as a very thin film on strong assist, ease of instruction within the laboratory, and so on. Its absorption spectrum overlaps with the sun spectrum and therefore opens up the opportunity of using sun power as the source of irradiation. Some other benefit is that the photo catalytic properties of TiO₂ can be studied in the fixed mattress shape in addition to within the form of a suspension. Further, TiO₂-primarily based mixed oxide catalysts which includes TiO₂/In₂O₃ (Shchukin et.al. 2004) TiO₂/SiO₂ and TiO₂/ZrO₂ (Clark et.al. 1996), supported catalysts consisting of Pt/TiO₂ (Clark et.al 1996), Rh/TiO₂ and Ru/TiO₂ (Yesodharan et.al. 1984), and Titanium-based thin films (Calvo et.al

2001) have additionally been proved to be very good photo catalysts. Huge investigations have been stated at the photo catalytic degradation of organic compounds which includes chlorinated compounds, chloro- and nitro phenols, dyes, pesticides and fragrant compounds. Semiconductor mediated photo catalytic oxidation is becoming one of the viable environment-friendly strategies for the removal of trace natural pollutants, including insecticides in water. This paper gives the idea of the most important publications inside the location of the decontamination/detoxification of insecticides.

II. CHARACTERISTICS OF TiO₂ PHOTOCATALYSTS

TiO₂ has drawn extremely good attentions of researchers in photovoltaic and photo catalysis fields since Fujishima and Honda first observed the potential of TiO₂ in splitting of water below ultraviolet (UV) light (Peill et.al 1996). Crystalline shape of TiO₂ has been suggested as one of the elements affecting its photo catalytic property. TiO₂ can make use of natural UV radiation from daylight for photo catalysis because it has suitable active separation among its conduction and valence band (Bideau et.al 1995). Band-hole energy of TiO₂ (3.2 eV for anatase; 0.03 for rutile) is fairly smaller in comparison to other semiconductors, together with ZnO (3.35 eV) and SnO₂ (3.6 eV) (Brandi et.al 2000). Therefore, TiO₂ is capable of soak up photons energy in the near UV variety ($h < 387$ nm). Photo catalytic reaction is initiated with the sufficient enter of radiation identical or better than the band-hole electricity of the goal semiconductor which reasons molecular excitation and charge separation. As end result, mobile electrons and holes can be generated and migrate to the surface of the semiconductor to take part inside the photo catalytic response (Dionysiou et.al 2000).

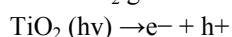
III. MECHANISM OF PHOTO CATALYTIC REACTION

The heterogeneous photo catalytic reaction is initiated with the absorption of radiation equal to or better than the band-gap strength of the target semiconductor. Energy band gap is defined because the distinction between the filled VB and the empty CB; in this case TiO₂ has a band-hole of 3.2 eV inside the form of anatase or 3.0 eV as rutile. When photons with strength identical to or higher than Energy band gap attain the surface of the photo catalyst, they'll reason molecular excitation. As a result, cell electrons will be generated inside the better-power CB simultaneously with the era of superb holes inside the decrease-energy VB of the photo catalyst. After the initiation of photo generated electron-hole pairs, the photo catalytic reaction will proceed through a chain of chemical activities. The photogenerated holes and electrons can either recombine and expend the absorbed power as warmness or be available to be used inside the redox response. Photogenerated holes and electrons that do not recombine migrate to the surface of catalyst for redox reaction. The redox response will make use of each the electron and hole, with the effective holes (h^+) for oxidation approaches and the electrons (e^-) for reduction tactics at the surface of the photo catalysts.

The highly reactive holes spoil apart the water molecule to form hydron (fine hydrogen cation, H^+ and the hydroxyl radical (OH^\bullet)). This OH^\bullet will then cause the release of strong oxidizing HO^\bullet radicals. Meanwhile, the electrons react with the oxygen molecule to shape a superoxide anion ($O_2^{\bullet-}$). This superoxide anion also produces HO^\bullet radicals through the formation of HO_2^\bullet radicals and H_2O_2 . The electron-hollow recombination step is unwanted because it will bring about procedure inefficiencies and waste the energy provided by way of the photon. Consequently, it's far regularly taken into consideration as one of the important factors restricting the efficiency of the photo catalytic processes. Besides, it's far determined that HO^\bullet is the maximum reactive radical species in TiO₂ aqueous suspension and the reaction of HO^\bullet with organic pollution is the maximum crucial step that leads to the mineralization of organic pollution. The heterogeneous photo catalytic reaction can essentially be represented via some of mechanistic steps. The overall mechanism of the photo catalytic reaction on light-illuminated TiO₂ is summarized in following reactions (Bideau et.al 1995; Ranjit et. al 1997).

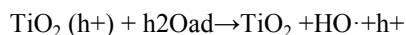
General mechanism of the photocatalytic reaction on illuminated TiO₂.

Photo-excited TiO₂ generates electron-hole pairs ($h\nu \geq EG$)

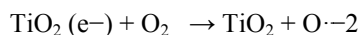


Photogenerated holes, h^+ migrate to catalyst surface and react with water molecules adsorbed on the catalyst surface

H₂O₂



Photogenerated electrons, e^- migrate to catalyst surface and molecular oxygen acts as an acceptor species in the electron-transfer reaction



Reactions of superoxide anions, $\text{O}_2^{\cdot -}$

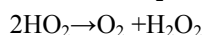
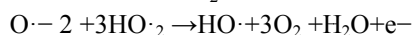
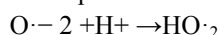
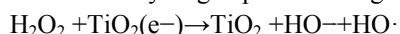
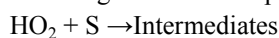


Photo conversion of hydrogen peroxide to give more $\text{HO}\cdot$ free-radical groups



Oxidization of organic adsorbed pollutants (Sad) by $\text{HO}\cdot$ onto the surface of the TiO_2



Overall reaction

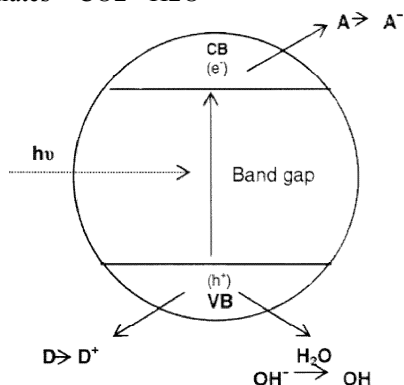
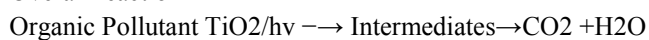


Figure 1: Schematic representation of the photochemical activation of a semiconductor and formation of the hydroxyl radical, VB: valence band; CB: conduction band; A: electron acceptor compound; D: electron donating compound.

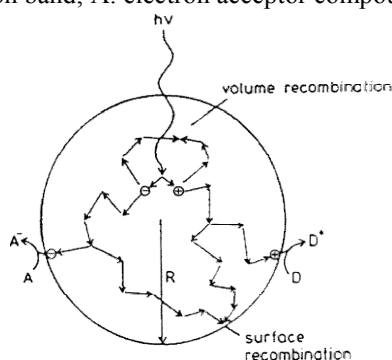


Figure 2: Fate of electrons and holes within a spherical particle of TiO_2 in the presence of acceptor A and donor D (Ollis et.al 1999).

Photocatalytic Degradation of Pesticide Contaminants in Water

The sources of this contamination may be summarized as follows:

1. Pesticide treatment as routine agricultural practice;
2. Rinse water polluted with pesticides from containers and spray equipment;
3. Wastewater from agricultural industry (cleaning or post-harvest treatment of fruits and vegetables) and
4. Plant residues contaminated with pesticides.

Most of these emerge as in the end in polluting water bodies with insecticides. The inherent hazards of traditional decontamination techniques have brought on scientists to take a look at the opportunity of the use of the advance oxidation method (AOP) based totally on photocatalysis. Each heterogeneous photocatalysis by way of semiconductors along with TiO₂ and homogeneous catalysis through photofenton had been tested on this context. Most of the photocatalytic research, stated to this point on this field, are briefly reviewed right here. For convenience of reference, the insecticides are classified in step with their chemistry (OP, organochlorine, and many others.) in addition to the chief mode of movement (pesticides, herbicides, etc.).

OP Insecticides

The photocatalytic degradation of many natural compounds in water is very effective in the in entire mineralization, the mechanism leading to the manner is not that simple NMR (1H and 31P) spectroscopic measurements in combination with monitoring pH and UV spectra have also been proved to be an effective tool to observe the degradation of fenitrothion and become aware of the intermediates. Research at the degradation of fenitrothion on polyoxometallate (PW12O₃—) photocatalysts additionally showed complete mineralization and the similarity of the intermediates advised that the mechanism is same as with TiO₂ catalysts.

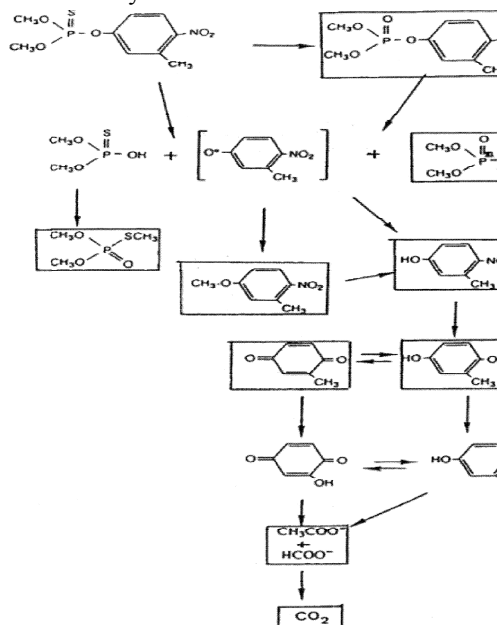


Figure 3: Schematic photocatalytic degradation pathway of fenitrothion (The enclosed molecules correspond to those detected) (Herrmann et.al 1999).

From a have a look at of the photooxidation of five OP pesticides, i.e. methamidophos, phorate, malathion, diazinon and EPN in UV–TiO₂, UV–H₂O₂ and UV–TiO₂–H₂O₂ systems, concluded that the reaction follows apparent first-order kinetics and the degradation efficiencies expanded in the order of phorate4methamidophos4malathion diazinon4EPN. The photooxidation of methamidophos and phorate changed into normally because of direct photolysis, probable due to the low bond power of P–S and C–S bonds. The degradation of malathion, diazinon and EPN is more often than not because of the oblique action of illuminated TiO₂. The observe indicated that a aggregate of H₂O₂ and TiO₂ below near UV illumination suggests lots promise in the photodegradation of OP pesticides and their eventual detoxification in water.

Several studies have indicated that the degradation rates of various organic contaminants such as OP pesticides over illuminated TiO₂ fitted the Langmuir–Hinshelwood kinetics (Tapalov et.al 1999; Konstantinou et. al 2001). The remark by using Kerzhentsev et al. ,that the primary products formed at some stage in the photocatalytic degradation of OP insecticides are oxon derivatives, is supported with the aid of Konstantinou et al, who showed that, in the case of

dichlofenthion and bromophos, the oxidant assault of the dOH on the P=S bond occurred first, resulting within the formation of bromoxon and dichlofenoxon. The non-stop assault of dOH accompanied via the rupture of the P–O bond consequences in the formation of the corresponding phenol and dialkyl phosphates (Pignatello et.al 1995)

The photocatalytic degradation pathways for dichlofenthion and bromophos methyl in aqueous solution are proposed as in Figs. 2 and 3. Which is Based on the spectroscopic identification of various degradation products.

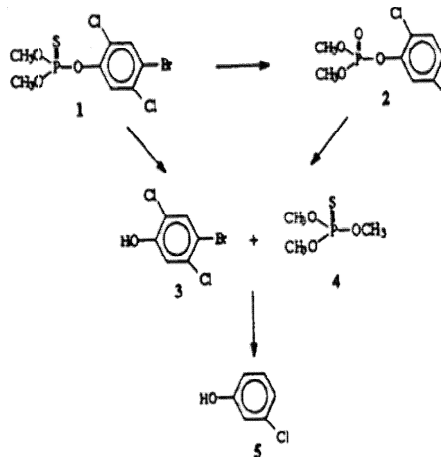


Figure 4: Proposed photodegradation pathway of dichlofenthion in aqueous solutions by TiO₂ and simulated solar light (Konstantinou et. al 2001).

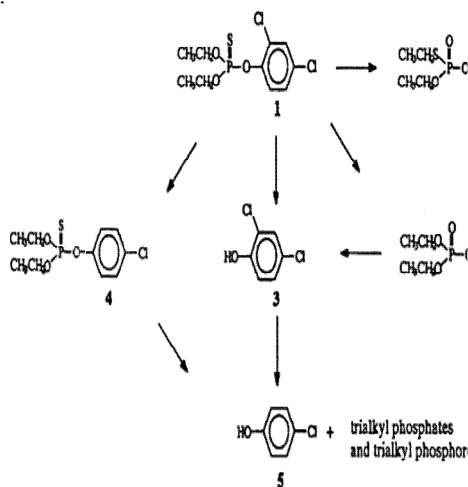


Figure 5: Proposed photodegradation pathway of bromophos methyl in aqueous solutions by TiO₂- simulated solar light (Konstantinou et. al 2001)

Photocatalytic mineralization research on malathion (Muzkat et.al 1998), in contaminated rinse water from agricultural sprayers and nicely-water showed that the 1/2-life time of solar photomineralisation within the one hundred ppb to 50 ppm attention range become less than 1 h in the presence of TiO₂ and the absence of delivered H₂O₂. Evaluation of the reaction in open and polyethylene film covered vessels showed that efficient photodegradation came about in sealed structures as properly. Ku and Jung studied the photocatalytic degradation of monocrotophos dimethyl (E)-l-methyl-2-(methylcarbamoyl) vinyl phosphate in aqueous solution through UV/TiO₂ under various pH values, catalyst dosages, mild intensities, dissolved oxygen stages and different operating conditions. The presence of oxygen enhances the decomposition of monocrotophos and inhibits the recombination of electrons and holes. Excess of oxygen had no similarly effect. The degradation charge become extra significant in acidic conditions than in alkaline situations. increase in light depth considerably increases the degradation price, till an top of the line mild depth turned into reached. The degradation leads to complete mineralization forming PO₃[—] and NO[—] ions, CO₂ and water.

The presence of anions together with CO₂—; SO₂—; PO₃— and NO— and cations including Ca²⁺, Mg²⁺ and Fe³⁺ was found to influence the charge of deterioration, the effect being depending on quite a number of things consisting of the nature of the pollutant, pH of the gadget as well as type and nature of the catalyst. An interesting observation changed into the simultaneous formation and decomposition of H₂O₂, ensuing in periodic increase and reduce in its attention. The use of photocatalysis as a tool for whole mineralization of OP compounds turned into in addition illustrated through the use of OP simulants of chemical change (Kozlova et. al 2004)

IV. CONCLUSION

The photocatalytic degradation of those organic pollutants the usage of titanium dioxide is the most broadly studied technique of overcoming the trouble of water contamination with the aid of organic pollutants. In this study we've mentioned several state of the artwork TiO₂ catalytic structures for decontaminating numerous insecticides and organic pollutants. Such structures have the potential to make a main impact on human fitness and safety through domestic and industrial use. However, anatase TiO₂ nevertheless famous a high charge of electron-hole recombination that prevents further enhancements in photocatalytic degradation performance. Structure of those unique TiO₂ complexes were investigated exclusively in labs, but limited investigations into the relevance of this technology in industry applications have been mentioned. Future work ought to build at the optimization of those systems and attention at the programs.

REFERENCES

- [1]. D. Bahnemann, J. Cunningham, M.A. Fox, E. Pelizzetti, N. Serpone, in: G.R. Helz, R.G. Zepp, D.G. Crosby (Eds.), *Aquatic and Surface Photochemistry*, Lewis Publishers, Boca Raton, FL, 1994, pp. 261–316.
- [2]. A. Vidal, *Chemosphere* 36 (1998) 2593–2606.
- [3]. D.F. Ollis, H. Al-Ekabi, *Photocatalytic Purification of Water and Air*, Elsevier, Amsterdam, 1993.
- [4]. J.-M. Herrmann, *Catal. Today* 53 (1999) 115–129.
- [5]. I.K. Konstantinou, T.A. Albanis, *Appl. Catal. B* 42 (2003) 319–335.
- [6]. S. Yesodharan, M. Gratzel, *Ber. Bunsenges. Phys. Chem.* 89 (1985) 121–126.
- [7]. H. Yin, Y. Wada, T. Kitamura, S. Yanagida, *Environ. Sci. Technol.* 35 (2001) 227–231.
- [8]. C. Kormann, D.W. Bahnemann, M.R. Hoffmann, *J. Photochem. Photobiol. A* 48 (1989) 161–169.
- [9]. J.K. Leland, A.J. Bard, *J. Phys. Chem.* 91 (1987) 5076–5083.
- [10]. S. Yesodharan, V. Ramakrishnan, J.C. Kuriacose, *Indian J. Chem.* 19A (1980) 402–406.
- [11]. A. Pruden, D.F. Ollis, *Environ. Sci. Technol.* 17 (1983) 628–631.
- [12]. A. Sclafani, L. Palmisano, E. Davis, *J. Photochem. Photobiol. A* 58 (1990) 113–123.
- [13]. E. Pramauro, M. Vincenti, V. Augugliaro, L. Palmisano, *Environ. Sci. Technol.* 27 (1993) 1790–1795.
- [14]. K.S. Wissiak, B. Sket, M. Vrtacnik, *Chemosphere* 41 (2000) 1451–1455.
- [15]. H. Yoneyama, Y. Yamashita, H. Tamura, *Nature* 282 (1979) 817–822.
- [16]. K. Kogo, H. Yoneyama, H. Tamura, *J. Phys. Chem.* 84 (1980) 1705–1713.
- [17]. Y. Yamashita, N. Aoyama, N. Takezawa, K. Yoshida, *Environ. Sci. Technol.* 34 (2000) 5211–5214.
- [18]. R. Abe, K. Shinohara, A. Tanaka, M. Hara, J.N. Kondo, K. Domen, *Chem. Mater.* 9 (1997) 2179–2184.
- [19]. M. Arai, *J. Phys. Chem. B* 105 (2001) 3289–3294.
- [20]. C. Anderson, A.J. Bard, *J. Phys. Chem. B* 101 (1997) 2611–2616.
- [21]. D. Shchukin, S. Poznyak, A. Kulak, P. Pichat, *J. Photochem. Photobiol. A* 162 (2004) 423–430.
- [22]. X. Fu, L.A. Clark, Q. Yang, M.A. Anderson, *Environ. Sci. Technol.* 30 (1996) 647–653.
- [23]. X. Fu, L.A. Clark, W.A. Zeltner, M.A. Anderson, *J. Photochem. Photobiol. A* 97 (1996) 181–186.
- [24]. S. Yesodharan, E. Yesodharan, M. Gratzel, *Sol. Energy Mater.* 10 (1984) 287–293.
- [25]. E. Yesodharan, M. Gratzel, *Helv. Chim. Acta.* 76 (1983) 2145–2156.
- [26]. M.E. Calvo, R.J. Candal, S.A. Bilmes, *Environ. Sci. Technol.* 35 (2001) 4132–4138.
- [27]. M.E. Zorn, D.T. Tompkins, W.A. Zeltner, M.A. Anderson, *Environ. Sci. Technol.* 34 (2000) 5206–5210.
- [28]. A. Tapalov, D. Molnar-Gabor, J. Csanadi, *Water Res.* 33 (1999) 1371–1376.

- [29]. R. Doong, W. Chang, J. Photochem. Photobiol. A 107 (1997) 239–244.
- [30]. J.C. D'Oliveira, G. Al-Sayyed, P. Pichat, Environ. Sci. Technol. 24 (1990) 990–996.
- [31]. N. Peill, M.R. Hoffmann, Environ. Sci. Technol. 30 (1996) 2806–2812.
- [32]. R.W. Matthews, S.R. McEvoy, J. Photochem. Photobiol. A 64 (1992) 231–246.
- [33]. M. Bideau, B. Claudel, C. Dubien, L. Faure, H. Kazouan, J. Photochem. Photobiol. A 91 (1995) 137–144.
- [34]. R.J. Brandi, O.M. Alfano, A.E. Cassano, Environ. Sci. Technol. 34 (2000) 2623–2639.
- [35]. D.D. Dionysiou, A.P. Khodadoust, A.M. Kern, M.T. Suidan, I. Baudin, J.M. Laine, Appl. Catal. B 24 (2000) 139–155.
- [36]. W.F. Jardim, S.G. Moraes, M.M.K. Takiyama, Water Res. 31 (1997) 1728–1732.
- [37]. K.T. Ranjit, B. Viswanathan, J. Photochem. Photobiol. A 108 (1997) 79–84.
- [38]. C.S. Turchi, D.F. Ollis, J. Catal. 119 (1989) 483–496.
- [39]. I.K. Konstantinou, T.M. Sakellariades, V.A. Sakkas, T.A. Albanis, Environ. Sci. Technol. 35 (2001) 398–405.
- [40]. J.J. Pignatello, Y. Sun, Water Res. 29 (1995) 1837–1844.
- [41]. L. Muzkat, L. Bir, J. Feigelson, J. Photochem. Photobiol. A 87 (1995) 85–88.
- [42]. Y. Ku, I.-L. Jung, Chemosphere 37 (1998) 2589–2597.
- [43]. E.A. Kozlova, P.G. Smirniotis, A.V. Vorontsov, J. Photochem. Photobiol. A 162 (2004) 503–511.