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# Photocatalytic Degradation of Organic Pollutants: Mechanisms and Kinetics

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## 1. Introduction

A wide variety of organic pollutants are introduced into the water system from various sources such as industrial effluents, agricultural runoff and chemical spills (Muszkat et al., 1994; Cohen et al., 1986). Their toxicity, stability to natural decomposition and persistence in the environment has been the cause of much concern to the societies and regulation authorities around the world (Dowd et al., 1998).

Development of appropriate methods for the degradation of contaminated drinking, ground, surface waters, wastewaters containing toxic or nonbiodegradable compounds is necessary. Among many processes proposed and/or being developed for the destruction of the organic contaminants, biodegradation has received the greatest attention. However, many organic chemicals, especially which are toxic or refractory, are not amendable to microbial degradation. Researcher showed their interest and started the intensive studies on heterogeneous photocatalysis, after the discovery of the photo-induced splitting of water on TiO<sub>2</sub> electrodes (Fujishima and Honda, 1972).

Semiconductor particles have been found to act as heterogeneous photocatalysts in a number of environmentally important reactions (Blake, 2001; Pirkanniemi, & Sillanpää, 2002; Gaya & Abdullah, 2008). Materials such as colloidal TiO<sub>2</sub> and CdS have been found to be efficient in laboratory-scale pollution abatement systems (Barni et al., 1995; Bellobono et al., 1994; Legrini et al., 1993; Mills & Hunte, 1997; Halmann, 1996), reducing both organic [e.g. halogenocarbons (Gupta & Tanaka, 1995; Martin et al., 1994; Read et al., 1996;), benzene derivatives (Blanco et al., 1996; Mao et al., 1996) detergents (Rao & Dube, 1996), PCB's (Huang et al., 1996), pesticides (Gianturco et al., 1997; Minero et al., 1996; Lobedank et al., 1997; Haque & Muneer 2003; Muneer & Bahnemann, 2002), explosives (Schmelling et al., 1996), dyes (Vinodgopal et al., 1996), cyanobacterial toxins (Liu et al., 2002)] and inorganic [e.g. N<sub>2</sub> (Ranjit et al., 1996), NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup> (Mills et al., 1994; Ranjit et al., 1995; Kosanic & Topalov, 1990; Pollema et al., 1992), cyanides (Mihaylov et al., 1993; Frank & Bard 1977), thiocyanates (Draper & Fox, 1990), cyanates (Bravo et al., 1994), bromates (Mills et al., 1996) etc.] pollutants/impurities to harmless species. Semiconductor photocatalysts have been shown to be useful as carbon dioxide (Irvine et al., 1990) and nitrogen (Khan & Rao, 1991) fixatives and for the decomposition of O<sub>3</sub> (Ohtani et al., 1992), destruction of micro-organisms such as bacteria (Matsunaga & Okochi, 1995; Zhang et al., 1994; Dunlop et al.,

2002), viruses (Lee et al., 1997), for the killing of malignant cancer-cells (Kubota et al., 1994), for the photo splitting of water (Pleskov & Krotova, 1993; Grätzel, 1981), for the cleanup of oil spills (Gerisher & Heller, 1992; Berry & Mueller, 1994), and for the control of the quality of meat freshness in food industry (Funazaki et al., 1995). Photocatalytic semiconductor films have been studied for the purposes of laboratory scale up of some of the above applications (Dunlop et al., 2002; Byrne et al., 2002) and, in the case of  $\text{TiO}_2$  films, for their photo-induced wettability properties (Wang et al., 1998, 1999; Sakai et al., 1998; Yu et al., 2002). This latter phenomenon, termed superhydrophilicity, is being explored for applications in the development of self-cleaning and antifogging surfaces.

Our research group at the Department of Chemistry, Aligarh Muslim University, Aligarh, India in collaboration with the Institut fuer Technische Chemie, Leibniz Universität Hannover, Hannover, Germany, have been actively involved in studying the photocatalytic degradation of variety of priority organic pollutants in aqueous suspensions.

### 1.1 Mechanism of photooxidation process

The acceleration of a chemical transformation by the presence of a catalyst with light is called photocatalysis. The catalyst may accelerate the photoreaction by interaction with the substrate in its ground or excited state and/or with a primary photoproduct, depending upon the mechanism of the photoreaction and itself remaining unaltered at the end of each catalytic cycle. Heterogeneous photocatalysis is a process in which two active phases solid and liquid are present. The solid phase is a catalyst, usually a semiconductor. The molecular orbital of semiconductors has a band structure. The bands of interest in photocatalysis are the populated valence band (VB) and it's largely vacant conduction band (CB), which is commonly characterized by band gap energy ( $E_{bg}$ ). The semiconductors may be photoexcited to form electron-donor sites (reducing sites) and electron-acceptor sites (oxidising sites), providing great scope for redox reaction. When the semiconductor is illuminated with light ( $h\nu$ ) of greater energy than that of the band gap, an electron is promoted from the VB to the CB leaving a positive hole in the valence band and an electron in the conduction band as illustrated in Figure 1.

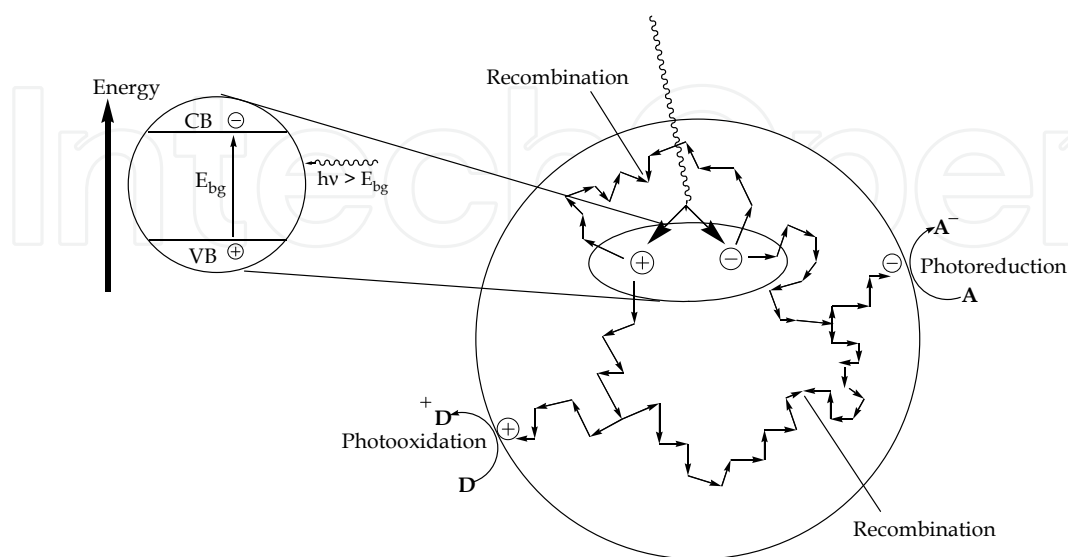


Fig. 1. Photoexcitation of semiconductor leading to charge separation / oxidation / reduction sites.

If charge separation is maintained, the electron and hole may migrate to the catalyst surface where they participate in redox reactions with sorbed species. Specially,  $h^+_{vb}$  may react with surface-bound  $H_2O$  or  $OH^-$  to produce the hydroxyl radical and  $e^-_{cb}$  is picked up by oxygen to generate superoxide radical anion ( $O_2^{\cdot-}$ ), as indicated in the following equations 1-3;

- absorption of efficient photons by titania ( $h\nu \geq E_{bg} = 3.2 \text{ eV}$ )



- formation of superoxide radical anion



- neutralization of OH group into  $\cdot OH$  by the hole



It has been suggested that the hydroxyl radical ( $\cdot OH$ ) and superoxide radical anions ( $O_2^{\cdot-}$ ) are the primary oxidizing species in the photocatalytic oxidation processes. These oxidative reactions would results in the degradation of the pollutants as shown in the following equations 4-5;

- oxidation of the organic pollutants via successive attack by  $\cdot OH$  radicals



- or by direct reaction with holes



For oxidation reactions to occur, the VB must have a higher oxidation potential than the material under consideration. The redox potential of the VB and the CB for different semiconductors varies between +4.0 and -1.5 volts versus Normal Hydrogen Electrode (NHE) respectively. The VB and CB energies of the  $TiO_2$  are estimated to be +3.1 and -0.1 volts, respectively, which means that its band gap energy is 3.2 eV and therefore absorbs in the near UV light ( $\lambda < 387 \text{ nm}$ ). Many organic compounds have a potential above that of the  $TiO_2$  valence band and therefore can be oxidized. In contrast, fewer organic compounds can be reduced since a smaller number of them have a potential below that of the  $TiO_2$  conduction band.

## 1.2 Use of semiconductor ( $TiO_2$ ) in various fields

Due to non-toxic, easily available, inexpensive, biologically and chemically inert and stable to photo and chemical corrosion,  $TiO_2$  is used in various fields as shown in Figure 2.

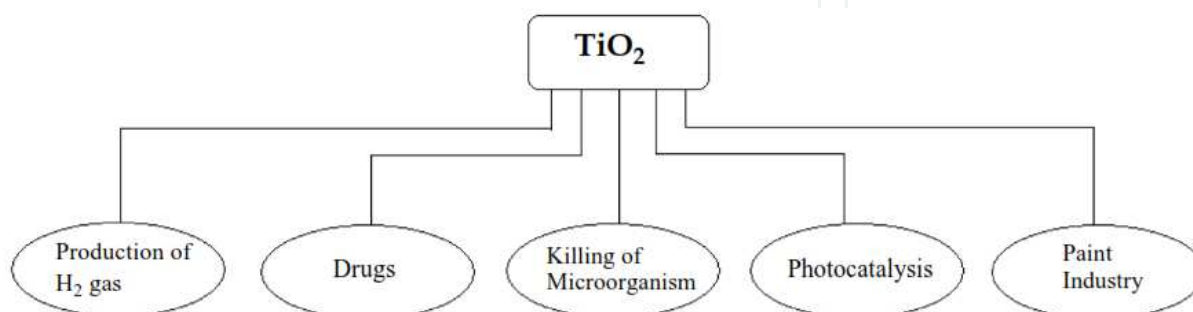


Fig. 2. Application of  $TiO_2$  in various fields.

The process of photocatalysis is also widely being contributed to various sub-discipline of Chemistry as shown in Figure 3.

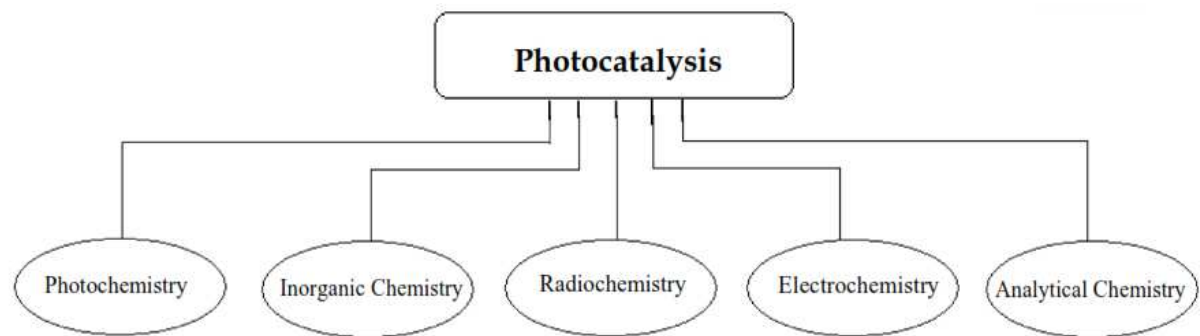


Fig. 3. Application of photocatalysis in various sub-divisions of Chemistry.

1.3 Our research focus

We have studied the photocatalysed degradation of a large variety of organic pollutants under different reaction conditions to determine the detailed degradation kinetics and product identification in few selected systems for better mechanistic understanding. The different class of organic pollutants studied by our research group are shown below in chart 1.

S. No.	Compound Studied	Reference
1	Dinoterb	2011; Dar et al., Res. Chem. Intermed., DOI 10.1007/s11164-011-0299-6
2	Fenoprop and Dichloroprop-P	2010; Faisal et al., Adv. Sci. Lett. 3, 512,
3	Acetamiprid	2010; Khan et al., Desalination, 261, 169.
4	Glyphosate	2008; Muneer & Boxall, Int. J. Photoenergy, article ID 197346
5	4-chlorophenoxyacetic acid	2007; Singh et al., J. Hazard. Mat., 142, 374.
6	Phenoxyacetic acid and 2,4,5-trichlorophenoxyacetic acid	2007; Singh et al., J. Mol. Catal. A: Chem., 264, 66.
7	Uracil and 5-bromouracil	2007; Singh et al., J. Hazard. Mat., 142, 425.
8	4-bromoaniline, 3-nitroaniline, pentachlorophenol, 1,2,3-trichlorobenzene and diphenylamine	2007; Abu Tariq et al., J. Mol. Catal. A: Chem., 265, 231.
9	Chlorotoluron	2006; Haque et al., Environ. Sci. Technol., 40, 4765.
10	Trichlopyr and Daminozid	2006; Qamar et al., J. Environ. Manag., 80, 99.

11	Acephate	2005; Atiqur Rahman et al., J. Adv. Oxid. Technol., 9, 1.
12	Dichlorvos and Phosphamidon	2005; Atiqur Rahman & Muneer, Desalination, 181, 161.
13	Propham, Propachlor and Tebuthiuron	2005; Muneer et al., Chemosphere, 61, 457.
14	Dichlone, 2-amino-5-chloropyridine, benzoyl peroxide and 3-chloro perbenzoic acid	2005; Qamar et al., Res. Chem. Intermed., 31, 807.
15	2,2'-dinitro biphenyl , N,N'-dimethyl-4-nitroso aniline , 4-dimethyl amino benzaldehyde, phthalaldehyde and tetramethyl benzoquinone	2005; Muneer et al., Appl. Catal. A: General, 289, 224.
16	Indole-3-acetic acid and Indole-3-butyric acid	2005; Qamar & Muneer, J. Hazard. Mat., 120, 219.
17	Thiram	2005; Haque & Muneer, Indian J. Chem. Technol., 12, 68.
18	Picloram, Dicamba and Floumeturon	2005; Atiqur Rahman & Muneer, J. Environ. Sci. & Health, B40, 257.
19	2,4-dichlorophenoxy Acetic Acid	2004; Singh & Muneer Res. Chem. Intermed., 30, 317.
20	Maleic Hydrazide	2004; Singh et al., J. Adv. Oxid. Tech., 7, 184.
21	Methoxychlor, Chlorothalonil and Disulfoton	2004; Muneer et al., Res. Chem. Intermed., 30, 663.
22	Dimethyl Terephthalate	2003; Atiqur Rahman et al., Res. Chem. Intermed., 29, 35.
23	Isoproturon	2003; Haque & Muneer, J. Environ. Manag., 69, 169.
24	Bromacil	2003; Singh et al., Photochem. Photobiol. Sci., 2, 151.
25	Diphenamid	2003; Atiqur Rahman et al., J. Adv. Oxid. Technol., 6, 100.
26	Benzidine and 1,2-diphenyl hydrazine	2002; Muneer et al., Chemosphere, 49, 193.
27	Terbacil and 2,4,5-tribromoimidazole	2002; Muneer & Bahnemann, Appl. Catal. B: Environ., 36, 95.
28	1,2-diethylphthalate	2001; Muneer et al., J. Photochem. Photobiol., A: Chem., 143, 213.
29	Diuron	1999; Muneer et al., Res. Chem. Intermed., 25, 667.

Chart 1.



The following text describes the results of the photocatalysed degradation of different pollutants under variety of conditions for degradation kinetics and product identification.

#### 1.4 Procedure for conducting the degradation experiments

Stock solutions of the pollutants containing the desired concentration were prepared in double distilled water. An immersion well photochemical reactor made of Pyrex glass equipped with a magnetic stirring bar, water circulating jacket and an opening for supply of molecular oxygen was used. A simplified diagram of the reactor system is shown in Figure 4.

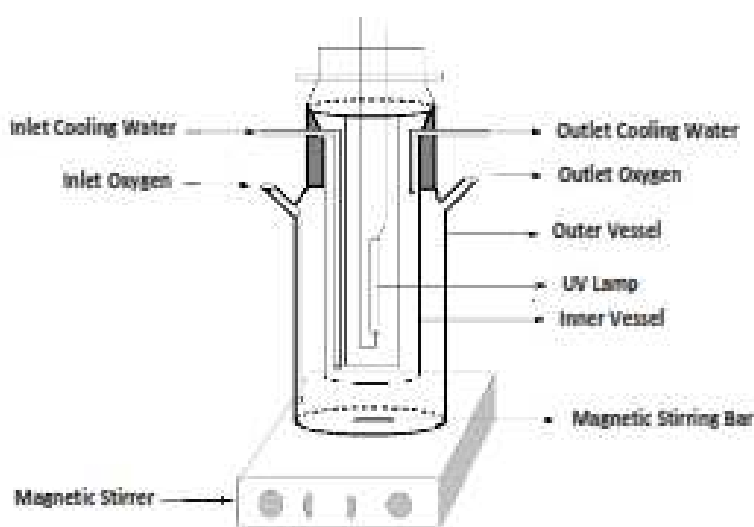


Fig. 4. Simplified diagram of Photochemical Reaction Vessel.

For irradiation experiment an aqueous solution of the pollutants with desired concentration is taken into the photoreactor and required amount of photocatalyst was added. Then the solution was stirred and bubbled with molecular / atmospheric oxygen for at least 15 minutes in the dark to allow equilibration of the system so that the loss of compound due to adsorption can be taken into account. The zero time reading was obtained from blank solution kept in the dark in the presence of  $\text{TiO}_2$  and oxygen but otherwise treated similarly to the irradiated solution. The suspensions were continuously purged with molecular / atmospheric oxygen throughout each experiment. Irradiations were carried out using medium pressure mercury lamp. The light intensity was measured using UV-light intensity detector. IR-radiation and short-wavelength UV-radiation were eliminated by water circulating Pyrex glass jacket. Samples (10 mL) were collected before and at regular intervals during irradiation and analyzed after centrifugation.

The sunlight experiments were carried out between 9:00 A.M to 2:30 P.M. on a sunny day. The light intensity was measured using UV-light intensity detector (Lutron UV-340), which was found to be in the range of 0.370 to 0.480 mW/cm<sup>2</sup>. Reactions were carried out in the same reaction vessel as described above. Aqueous solution of desired concentration of the model compound containing required amount of photocatalyst was taken and stirred for 15 min. in the dark in presence of oxygen for equilibration. The solution was then placed on flat

platform under sunlight with continuous stirring and purging of molecular oxygen. Samples (10 mL) were collected before and at regular intervals during the illumination and analyzed after centrifugation.

## 2. Analysis

### 2.1 Photomineralization of organic pollutants

The photomineralization of the pesticide was measured using Total Organic Carbon analyzer (Shimadzu TOC 5000 A). The main principle of TOC analyzer involves the use of carrier gas (oxygen), which is flow-regulated (150 ml / min) and allows to flow through the total carbon (TC) combustion tube, which is packed with catalyst, and kept at 680<sup>o</sup> C. When the sample enters the TC combustion tube, TC in the sample is oxidized to carbon dioxide. The carrier gas containing the combustion products from the TC combustion tube flows through the inorganic carbon (IC) reaction vessel, dehumidifier, halogen scrubber and finally reaches the sample cell of the nondispersive infrared (NDIR) detector which measures the carbon dioxide content. The output signal (analog) of the NDIR detector is displayed as peaks. The peak areas are measured and processed by the data processing unit. Since the peak areas are proportional to the total carbon concentration, the total carbon in a sample may be easily determined from the calibration curve prepared using standard solution of known carbon content. Total carbon is the sum of TOC (Total Organic Carbon) and IC (Inorganic Carbon).

### 2.2 Photodegradation of the pesticide

The photodegradation of the pesticide was measured using UV-Vis spectrophotometry or HPLC analysis techniques.

### 2.3 Characterization of intermediate products

Intermediate product formed during the photooxidation process was characterized by monitoring the reaction as a function of time using GC/MS analysis technique. For GC/MS analysis a Shimadzu Gas Chromatograph and Mass Spectrometer (GCMS-QP 5050) equipped with a 25m CP SIL 19 CB (d=0.25mm) capillary column, operating temperature programmed (220<sup>o</sup>C for 40 min at the rate of 10<sup>o</sup>C min<sup>-1</sup>) in splitless mode injection volume (1.0 µL) with helium as a carrier gas was used.

## 3. Photocatalysis of organic pollutants under different conditions

### 3.1 In the presence of TiO<sub>2</sub>

Irradiation of an aqueous suspension of desired organic pollutants in the presence of TiO<sub>2</sub> lead to decrease in absorption intensity and depletion in TOC content as a function of time.

As a representative example Figure 5 shows the change in absorption intensity and depletion in TOC as a function of time on irradiation of an aqueous solution of isoproturon (0.5 mM, 250 ml) in the presence and absence of photocatalyst (Degussa P25, 1 gL<sup>-1</sup>) by the "Pyrex" filtered output of a 125 W medium Pressure mercury lamp (radiant flux 4.860 mW/cm<sup>2</sup>).



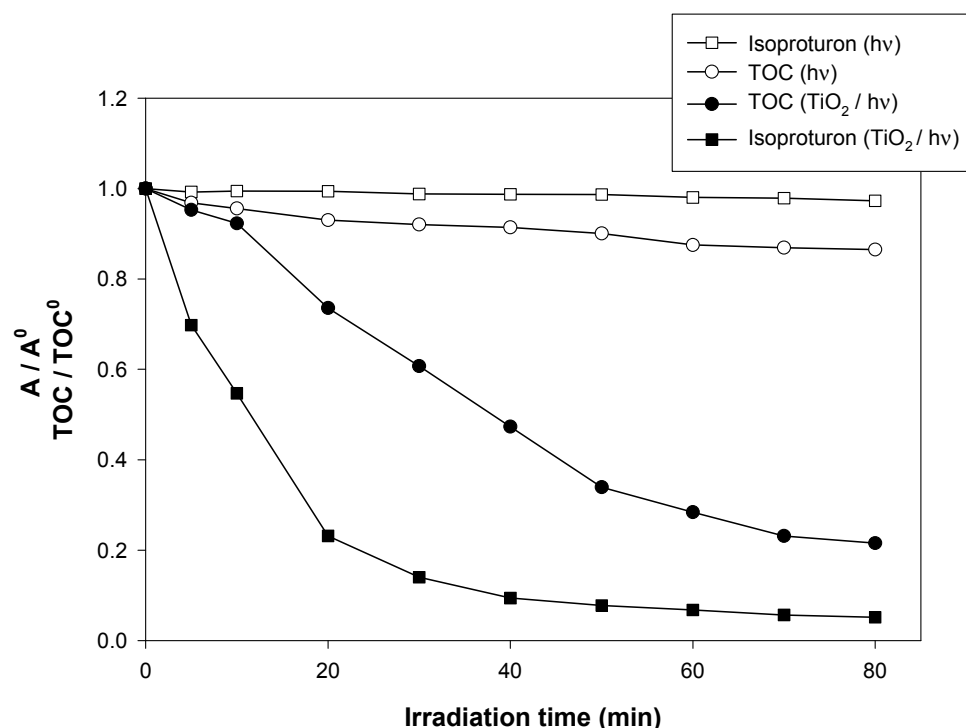


Fig. 5. Depletion in TOC and change in absorption intensity as a function of irradiation time for an aqueous solution of isoproturon in the presence and absence of the photocatalyst. Experimental conditions: 0.5 mM isoproturon,  $V=250$  mL, photocatalyst:  $\text{TiO}_2$  (Degussa P25,  $1 \text{ gL}^{-1}$ ), immersion well photoreactor, 125 W medium pressure Hg lamp, absorbance was followed at 238 nm after 75% dilution, cont.  $\text{O}_2$  purging and stirring, irradiation time = 80 min.

It could be seen that 94.8% degradation and 78.45 % mineralization of the isoproturon takes place after 80 min of illumination. On the other hand no observable loss of the compound was found when the irradiations were carried out in the absence of the photocatalysts (Haque & Muneer, 2003).

Both the mineralization (depletion of TOC Vs irradiation time) and decomposition (decrease in absorption intensity/concentration Vs irradiation time) curves can be fitted reasonably well by an exponential decay curve suggesting the first order kinetics. Figure 6 shows the linear regression curve fit for the natural logarithm of the degradation of isoproturon Vs irradiation time for first order reaction. For each experiment, the degradation rate constant was calculated from the plot of the natural logarithm of the TOC depletion or absorbance / concentration of the pesticide as a function of irradiation time (the concentration of the pollutant was calculated by taking the absorbance of the pollutant at its  $\lambda_{\text{max}}$  of standard concentration and then by plotting the graph of absorbance Vs standard concentration of the pollutant). The degradation rate for the mineralization and for the decomposition of the pollutants for first order reaction was calculated using formula given below;

$$-d[\text{TOC}]/dt = kc^n \quad (6)$$

$$-d[c]/dt = kc^n \quad (7)$$

TOC = Total Organic Carbon,  $k$  = rate constant,  $c$  = concentration of the pollutant,  $n$  = order of reaction.

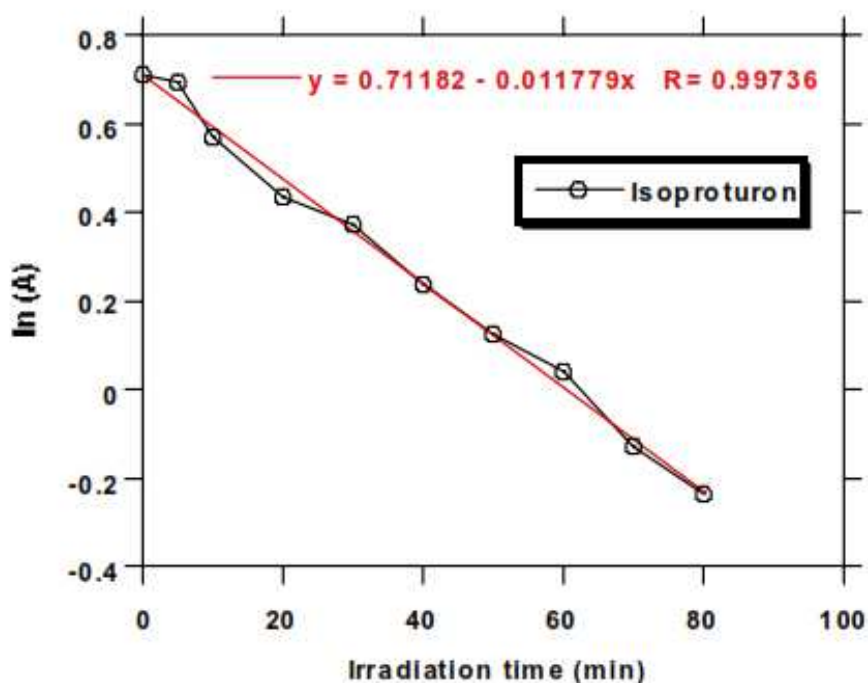


Fig. 6. Plot showing the linear regression curve fit for the natural logarithm of absorbance of the pesticide concentration of isoproturon against irradiation time for the first order reaction.

### 3.2 Comparison of different photocatalysts

Titanium dioxide is known to be the semiconductor with the highest photocatalytic activity and stable in aqueous solution. Several reviews have been written, regarding the mechanistic and kinetic details as well as the influence of experimental parameters. It has been demonstrated that degradation by photocatalysis can be more efficient than by other wet-oxidation technique (Weichrebe and Vogelpohl, 1995).

We have tested the photocatalytic activity of four different commercially available  $\text{TiO}_2$  powders (namely Degussa P25, Sachtleben Hombikat UV100, Milenium Inorganic PC500 and Travancore Titanium Product, India) on the degradation kinetics of the pollutants.

In most of the cases it has been observed that the degradation of pollutants under investigation proceed much more rapidly in the presence of Degussa P25 as compared with other  $\text{TiO}_2$  samples (Muneer and Bahnemann, 2001; Haque & Muneer, 2003; Bahnemann et al., 2007) as shown in Figure 7 (isoproturon). The better photocatalytic activity of Degussa P25 has also been reported by Pizzaro et al., in 2005. While in some cases Hombikat UV 100 is found to be better than Degussa P25 for the degradation of benzidine, eosine yellowish, and Remazol brilliant blue R (Muneer et al., 2002; Saquib and Muneer, 2002, 2003) as shown in Figure 8 (eosine yellowish). In an earlier study Lindner et al. 1995, showed that Hombikat UV100 was almost four times more effective than P25 when dichloroacetic acid was used as the model pollutant.

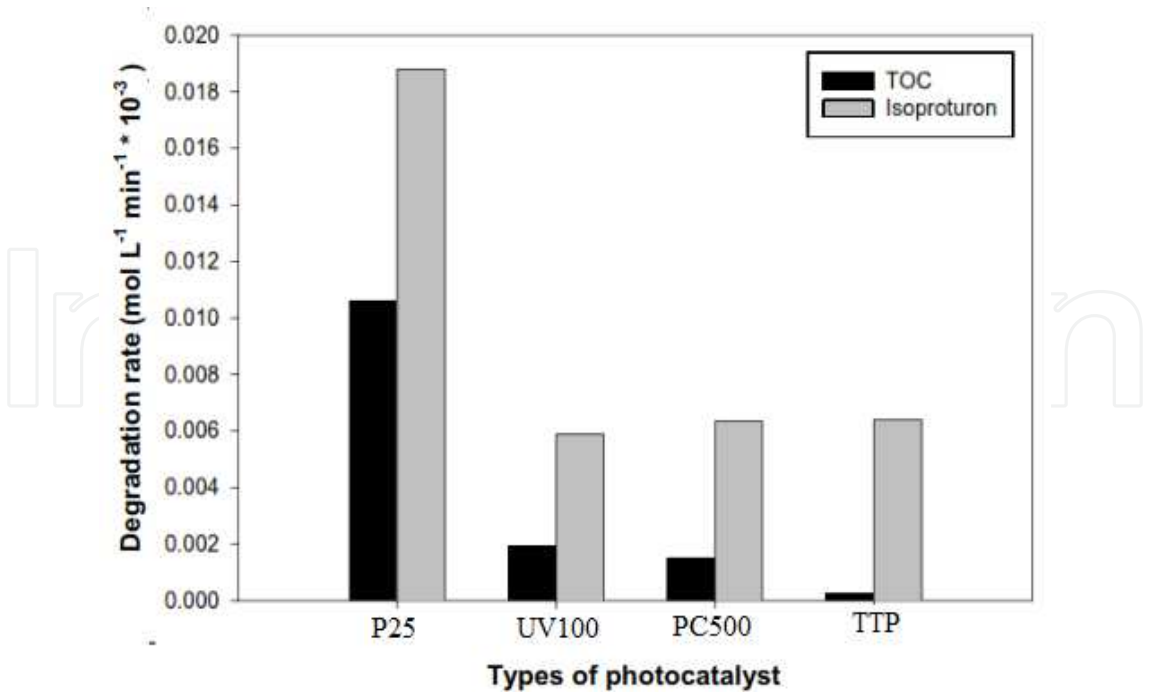


Fig. 7. Comparison of degradation rate for the mineralization and for the decomposition of isoproturon in the presence of different photocatalysts. Experimental conditions: 0.5 mM isoproturon, V=250 mL, photocatalysts: TiO<sub>2</sub> Degussa P25 (1 gL<sup>-1</sup>), Sachtleben Hombikat UV100 (1 gL<sup>-1</sup>), PC500 (1 gL<sup>-1</sup>), TTP (1 gL<sup>-1</sup>).

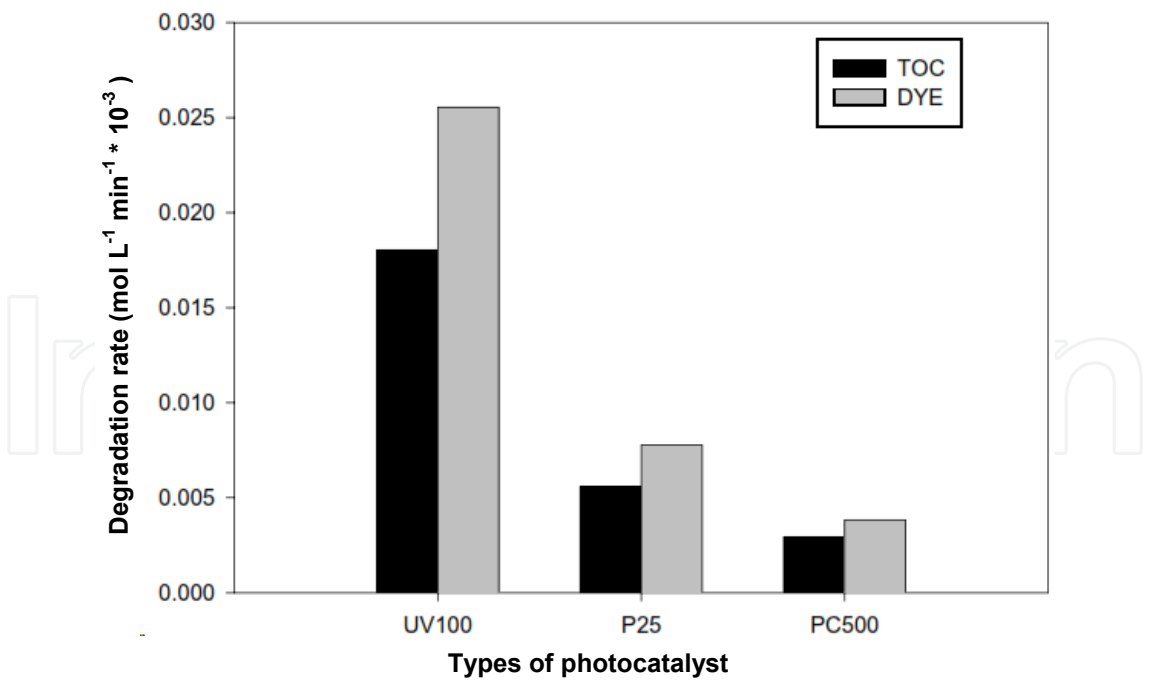


Fig. 8. Comparison of degradation rate for the mineralization and for the decomposition of eosine yellowish under different photocatalysts. Experimental conditions: 0.25 mM dye concentration, V=250 mL, photocatalysts: TiO<sub>2</sub> Degussa P25 (1 gL<sup>-1</sup>), Sachtleben Hombikat UV100 (1 gL<sup>-1</sup>) and PC500 (1 gL<sup>-1</sup>).

The differences in the photocatalytic activity of  $\text{TiO}_2$  are likely to be due to differences in the BET-surface, impurities, lattice mismatches or density of hydroxyl groups present on the catalyst's surface. Since they will affect the adsorption behaviour of a pollutant or intermediate molecule and the lifetime and recombination rate of electron-hole pairs.

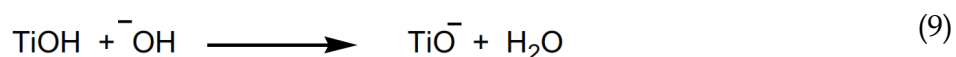
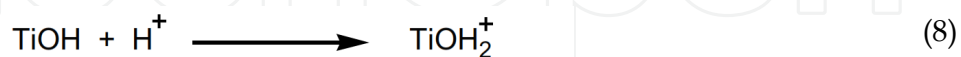
The reason for the better photocatalytic activity of Degussa P25, could be attributed to the fact that P25 being composed of small nano-crystallites of rutile being dispersed within an anatase matrix. The smaller band gap of rutile "catches" the photons, generating electron-hole pairs. The electron transfer, from the rutile conduction band to electron traps in anatase phase takes place. Recombination is thus inhibited allowing the hole to move to the surface of the particle and react (Hurum et al., 2003). The better efficiency of photocatalyst Degussa P25 may also due to 'quantum size effect' (Nozik et al., 1993; weller, 1993). When the particles become too small, there is a 'blue shift' with an increase of the band gap energy, detrimental to the near UV-photon absorption, and an increase of the electron-hole recombination.

### 3.3 Influence of pH on the degradation kinetics

An important parameter in the photocatalytic reactions taking place on the particulate surfaces is the pH of the solution, since it dictates the surface charge properties of the photocatalyst and size of aggregates it forms. Employing Degussa P25 as photocatalyst the decomposition and mineralization of pollutant in aqueous suspensions of  $\text{TiO}_2$  was studied as a function of pH.

The degradation rate for the decomposition and mineralization of acid red 29 was found to increase with the increase in pH from 3 to 11 as shown in Figure 9 (Qamar et al., 2005) while the degradation rate for the decomposition and mineralization of the pesticide derivative propachlor was found to decrease with the increase in pH from 3 to 11 as shown in Figure 10 (Muneer et al, 2005). Similar results on pH effect have also been reported earlier by Vaz et al., 1998 (for the degradation of uracil and 5-halogenouracil) and Lu et al., 1995 (for the degradation of dichlorvos, propoxur and 2,4-D).

The interpretation of pH effects on the photocatalytic process is very difficult task because of its multiple roles such as electrostatic interactions between the semiconductor surface, solvent molecules, substrate and charged radicals formed during the reaction process. The ionization state of the surface of the photocatalyst can be protonated and deprotonated under acidic and alkaline conditions, respectively, as shown in following equations:



The point of zero charge (pzc) of the  $\text{TiO}_2$  (Degussa P25) is widely reported at  $\text{pH} \sim 6.25$  (Augustynski, 1988). Thus, the  $\text{TiO}_2$  surface will remain positively charged in acidic medium ( $\text{pH} < 6.25$ ) and negatively charged in alkaline medium ( $\text{pH} > 6.25$ ). The functional group present on the pollutants can be protonated and deprotonated depending on the pH of the reaction mixture. The better degradation rate in acidic or basic pH may also be attributed on the basis of the fact that the structural orientation of the molecule is favoured for the attack of the reactive species under that condition.

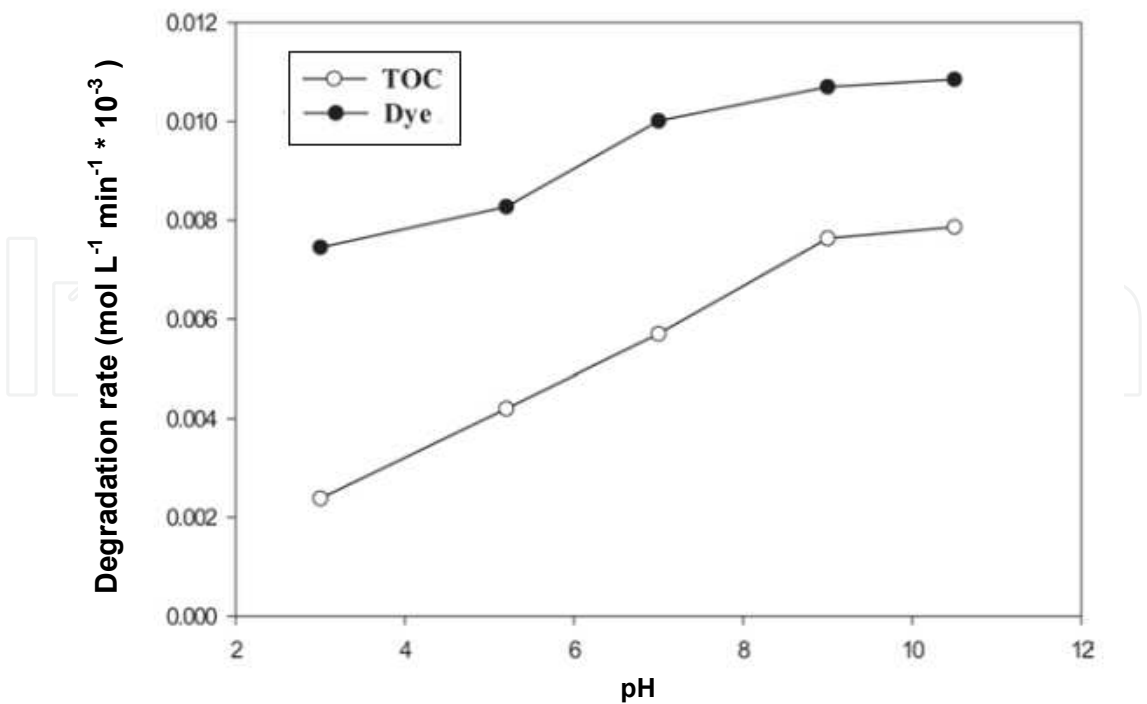


Fig. 9. Influence of pH on the degradation rate for the mineralization and for the decomposition of acid red 29. Experimental conditions: Reaction pH (3, 5.2, 7, 9 and 10.5), 0.25 mM dye concentration, V=250 mL, photocatalyst: TiO<sub>2</sub> (Degussa P25, 1 gL<sup>-1</sup>).

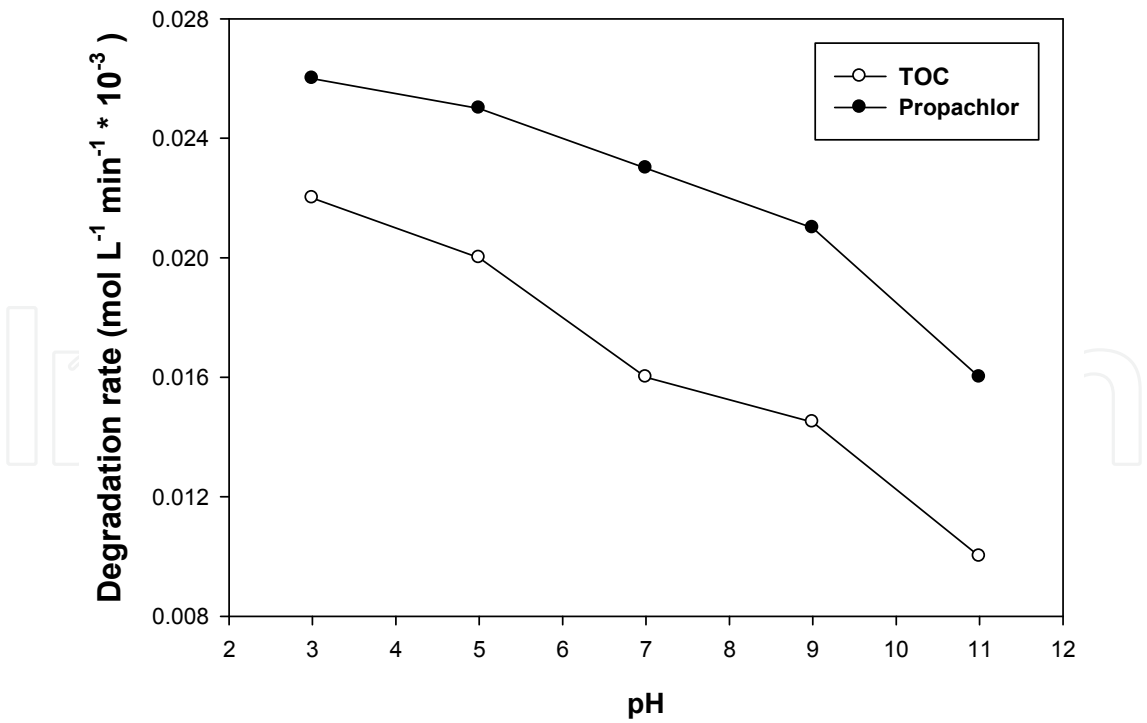


Fig. 10. Influence of pH on the degradation rate for the mineralization and for the decomposition of propachlor. Experimental conditions: Reaction pH (3, 5, 7, 9 and 11), 0.6 mM propachlor, V=250 mL, photocatalyst TiO<sub>2</sub> (Degussa P25, 1 gL<sup>-1</sup>).

### 3.4 Effect of substrate concentration

It is important both from mechanistic and from application point of view to study the dependence of substrate concentration in the photocatalytic reaction rate. Effect of substrate concentration on the degradation of the pollutants was studied at different concentrations. As a representative example Figure 11 shows the degradation rate for the TOC depletion and for the decomposition of pollutant as a function of substrate concentration employing Degussa P25 as photocatalyst (Muneer et al, 2005). It was found that the degradation rate for the decomposition and for the mineralization increases gradually with the increase in substrate concentrations. Similar trend was found in most of the colourless organic pollutants as reported earlier (Sabin et al., 1992; Krosley et al., 1993; O'Shea et al., 1997). In coloured compound it has been found that the degradation rate increase upto a certain limit and after that a further increase in substrate concentration lead to decrease in the degradation rate. This may be due to the fact that as the initial concentrations of the pollutant increases, the irradiating mixture becomes more and more intense which prevents the penetration of light to the surface of the catalyst. Hence, the generation of relative amount of  $\cdot\text{OH}$  and  $\text{O}_2^{\cdot-}$  on the surface of the catalyst do not increase as the intensity of light and irradiation times are constant. Conversely, their concentrations will decrease with increase in concentration of the pollutant as the light photons are largely absorbed and prevented from reaching the catalyst surface by the substrate molecules.

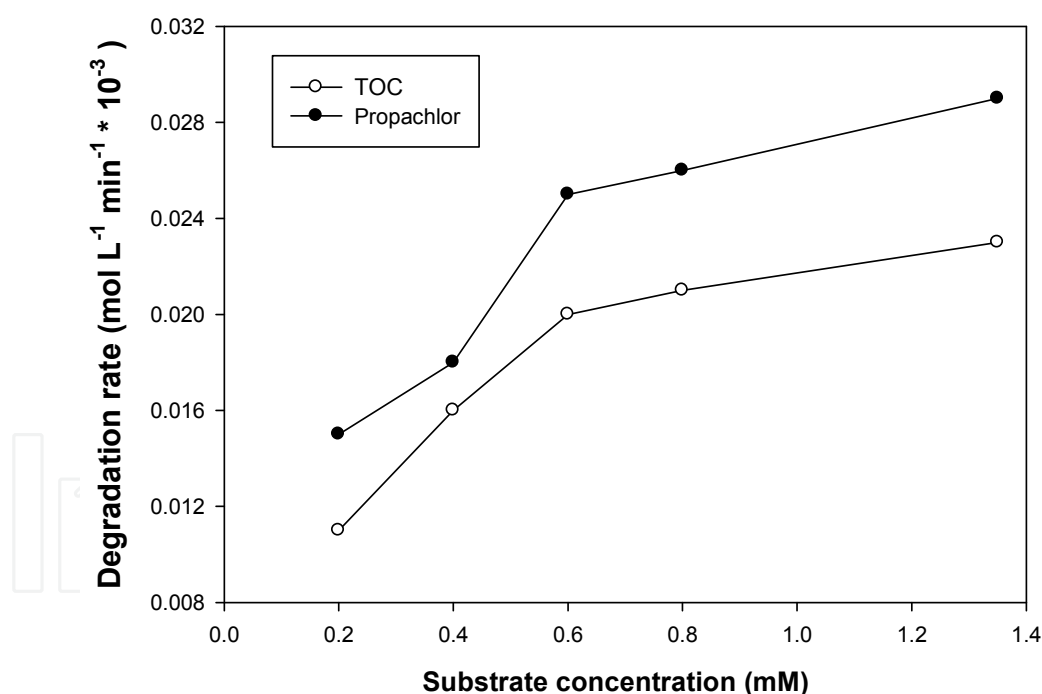


Fig. 11. Influence of substrate concentration on the degradation rate for the mineralization and for the decomposition of propachlor. Experimental conditions: Substrate concentrations (0.20, 0.40, 0.60, 0.80 and 1.35 mM), V=250 mL, photocatalyst:  $\text{TiO}_2$  (Degussa P25, 1  $\text{gL}^{-1}$ ).

As oxidation proceeds, less and less of the surface of the  $\text{TiO}_2$  particle is covered as the pollutant is decomposed. Evidently, at total decomposition, the rate of degradation is zero and a decreased photocatalytic rate is to be expected with increasing irradiation time. It has been agreed, with minor variation that the expression for the rate of photodegradation of



organic substrates with irradiated  $\text{TiO}_2$  follows the Langmuir Hinshelwood (L-H) law for the four possible situations, i.e., (1) the reaction takes place between two adsorbed substances, (2) the reaction occurs between a radical in solution and an adsorbed substrate molecule, (3) the reaction takes place between a radical linked to the surface and a substrate molecule in solution, and (4) the reaction occurs with both the species being in solution. In all cases, the expression for the rate equation is similar to that derived from the L-H model, which has been useful in modelling the process, although it is not possible to find out whether the process takes place on the surface, in the solution or at the interface. Our results, on the effect of the initial concentration on the degradation rate are in agreement with the assumption of the Langmuir Hinshelwood model.

### 3.5 Effect of catalyst concentration

The effect of photocatalyst concentration on the degradation kinetics of pollutant under investigation was studied employing different concentrations of Degussa P25 varying from 0.5 to 7.5  $\text{g L}^{-1}$ . As a representative example the degradation rate for the TOC depletion and for the decomposition of the tebuthiuron as function of catalyst loading is shown in Figure 12 (Muneer et al., 2005). It was observed that the degradation rate was found to increase with the increase in catalyst concentration upto 5  $\text{g L}^{-1}$  and on subsequent addition of catalyst lead to the levelling off the degradation rate.

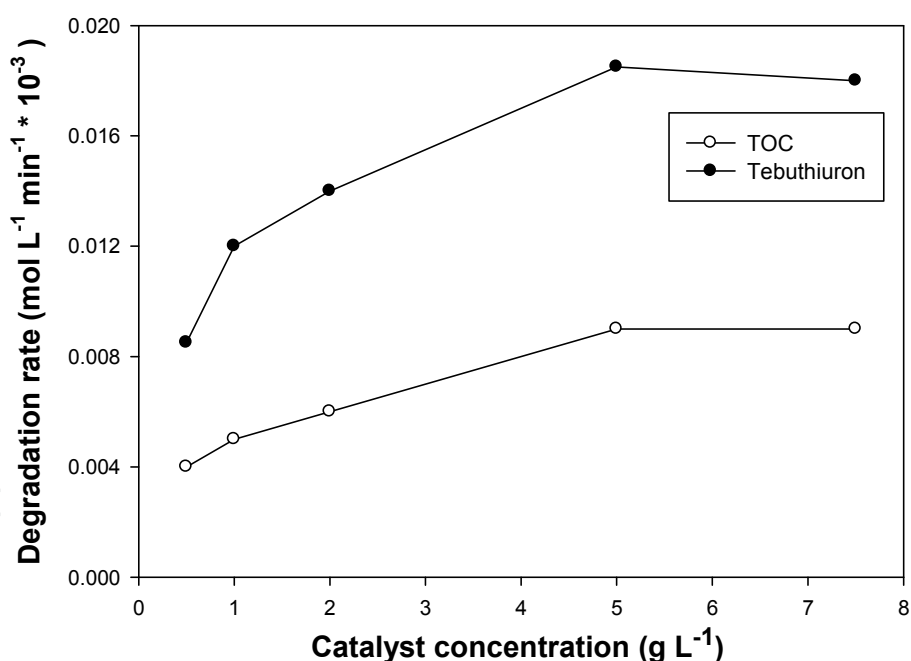


Fig. 12. Influence of catalyst concentration on the degradation rate for the mineralization and for the decomposition of tebuthiuron. Experimental conditions: Photocatalyst concentrations:  $\text{TiO}_2$  Degussa P25 (0.5, 1.0, 2.0, 5.0 and 7.5  $\text{g L}^{-1}$ ),  $V=250 \text{ mL}$ .

Whether in static, slurry, or dynamic flow reactors, the initial reaction rates were found to be directly proportional to catalyst concentration, indicating a heterogeneous regime. However, it was observed that above a certain concentration, the reaction rate decreases and becomes independent of the catalyst concentration. This limit depends on the geometry and working conditions of the photoreactor and for a definite amount of  $\text{TiO}_2$  in which all the

particles, i.e., surface exposed, are totally illuminated. When the catalyst concentration is very high, after travelling a certain distance on an optical path, turbidity impedes further penetration of light in the reactor. In any given application, this optimum catalyst concentration  $[(\text{TiO}_2)_{\text{OPT}}]$  has to be found, in order to avoid excess catalyst and insure total absorption of efficient photons. Our results on the effect of catalyst concentration on the degradation rate for the TOC depletion and decomposition of pollutants under investigation are in agreement with numerous studies reported in the literature (Shifu and Yunzhang 2007, Daneshvar et al., 2004).

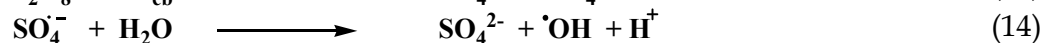
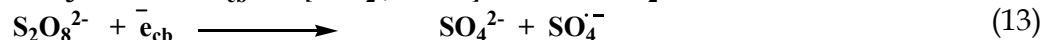
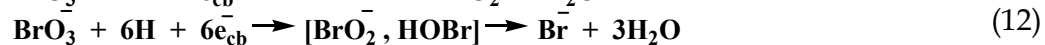
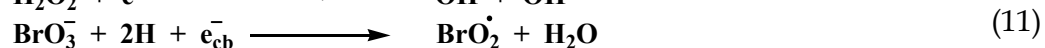
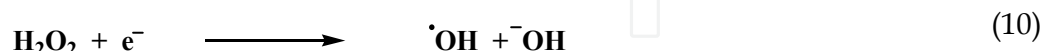
It is believed that both the number of photons absorbed as well as the solute molecules adsorbed increases with increase in number of  $\text{TiO}_2$  particles upto the optimum value. Any further increase in  $\text{TiO}_2$  concentration beyond optimum value may cause scattering and screening effects which reduces the specific activity of the catalyst (Evgenidou et al., 2007). The highly turbid suspension may prevent the catalyst farthest from being illuminated (Rahman and Muneer, 2005). Higher amount of catalyst may lead to aggregation of  $\text{TiO}_2$  particles which may decrease the catalytic activity (Garcia and Takashima, 2003). The optimum value of catalyst has been found to vary with different initial solute concentrations (Sakthivel et al., 2003).

### 3.6 Effect of different electron acceptors

One practical problem in using  $\text{TiO}_2$  as a photocatalyst is the undesired electron / hole recombination, which, in the absence of proper electron acceptor or donor, is extremely efficient and represent the major energy - wasting step thus limiting the achievable quantum yield. One strategy to inhibit electron - hole pair recombination is to add other (irreversible) electron acceptors to the reaction. They could have several different effects such as, i.e., (1) to increase the number of trapped electrons and, consequently, avoid recombination, (2) to generate more radicals and other oxidizing species, (3) to increase the oxidation rate of intermediate compounds and (4) to avoid problems caused by low oxygen concentration. In highly toxic wastewater where the degradation of organic pollutants is the major concern, the addition of electron acceptors to enhance the degradation rate may often be justified. With this view, the electron acceptor such as potassium persulphate, potassium bromate and hydrogen peroxide were added in the solution.

As a representative example Figure 13 shows the degradation rate for the mineralization and decomposition of the pollutants in the presence of different electron acceptors.

The electron acceptors such as hydrogen peroxide, bromate and persulphate ions are known to generate hydroxyl radicals by the mechanisms shown in equations 10-14;



The respective one-electron reduction potentials of different species are:  $E(\text{O}_2/\text{O}_2^{\cdot-}) = -155\text{mV}$ ,  $E(\text{H}_2\text{O}_2/\text{HO}\cdot) = 800\text{mV}$ ,  $E(\text{BrO}_3^-/\text{BrO}_2\cdot) = 1150\text{ mV}$ , and  $E(\text{S}_2\text{O}_8^{2-}/\text{SO}_4^{\cdot-}) = 1100\text{ mV}$  (Wardman, 1989). From the thermodynamic point of view all employed additives should therefore be more efficient electron acceptors than molecular oxygen.

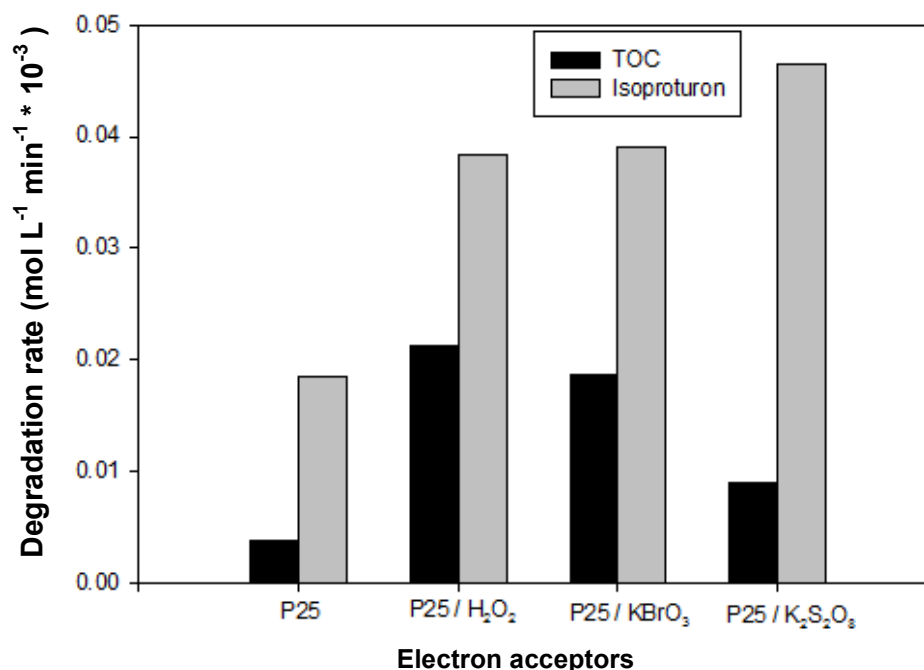


Fig. 13. Comparison of degradation rate for the mineralization and for the decomposition of isoproturon in the presence of different electron acceptors. Experimental conditions: Electron acceptors: KBrO<sub>3</sub> (5mM), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (5mM), H<sub>2</sub>O<sub>2</sub> (10mM), 1.5 mM isoproturon, V=250mL, photocatalyst: TiO<sub>2</sub> (Degussa P25, 1 g L<sup>-1</sup>).

The effective electron acceptor ability of KBrO<sub>3</sub> has been observed in number of studies before (Nevim et al., 2001; Muneer and Bahnemann, 2001). The reason can be attributed to the number of electrons it reacts as shown in eq. 12. Another possible explanation might be a change in the reaction mechanism of the photocatalytic degradation. Since the reduction of bromate ions by electrons does not lead directly to the formation of hydroxyl radicals, but rather to the formation of other reactive radicals or oxidizing agents eg. BrO<sub>2</sub><sup>-</sup> and HOBr. Furthermore, bromate ions by themselves can act as oxidizing agents. Linder has proposed a mechanism for the photocatalytic degradation of 4-chlorophenol in the presence of bromate ions considering direct oxidation of the substrate by bromate ions (Linder, 1997).

The enhanced effect of persulphate ion on the degradation of pollutants may be accounted on the basis that persulphate is a beneficial oxidizing agent in photocatalytic detoxification because SO<sub>4</sub><sup>-</sup> is formed from the oxidant by reaction with the electron generated at conduction band (e<sub>cb</sub>) of the semiconductor as shown in eq. 13. This sulphate radical anion (SO<sub>4</sub><sup>-</sup>) is a strong oxidant (E<sub>0</sub> = 2.6 eV) and it can react with the organic pollutants in three possible modes (1) by abstracting a hydrogen atom from saturated carbon, (2) by adding to unsaturated or aromatic carbon and (3) by removing one electron from the carboxylate anions and from certain neutral molecules. In spite of this sulphate radical anion can trap the photogenerated electrons and/ or generated hydroxyl radical as shown in eq. 14. The formation of sulphate radical anion and hydroxyl radical are powerful oxidant, which can degrade the organic pollutants at a faster rate.

The effect of H<sub>2</sub>O<sub>2</sub> has been investigated in numerous studies and it was observed that it increases the photodegradation rates of organic pollutants (Hallam, 1992). The enhancement of the degradation rate on addition of H<sub>2</sub>O<sub>2</sub> can be rationalized in terms of several reasons. Firstly, it increases the rate by removing the surface-trapped electrons,

thereby lowering the electron-hole recombination rate and increasing the efficiency of hole utilization for reactions such as ( $\cdot\text{OH} + \text{h}^+ \rightarrow \cdot\text{OH}$ ). Secondly,  $\text{H}_2\text{O}_2$  may split photolytically to produce hydroxyl radicals ( $\cdot\text{OH}$ ) directly, as cited in studies of homogeneous photooxidation using UV / ( $\text{H}_2\text{O}_2 + \text{O}_2$ ) (Peyton and Glaze 1988). Thirdly, the solution phase may at times be oxygen starved, because of either oxygen consumption or slow oxygen mass transfer, and peroxide addition thereby increases the reaction rate.

During the photocatalytic degradation the free radical formed serve a dual function. They are not only the strong oxidants but also at the same time their formation and subsequent rapid oxidation reactions inhibit the electron hole pair recombination.

### 3.7 Comparison of degradation rate under UV and sunlight

For practical applications of wastewater treatment based on these processes, the utilization of sunlight is preferred. Hence the aqueous suspension of  $\text{TiO}_2$  containing organic pollutants was exposed to solar radiation. As a representative example Figure 14 shows the change in concentration as a function of irradiation time on illumination of an aqueous suspension of acetamiprid (0.1 mM) in the presence of  $\text{TiO}_2$  (Degussa P25,  $1\text{gL}^{-1}$ ) under sunlight and UV light source (Khan et al., 2010). It was found that the degradation of the model compound proceeds reasonably fast under sunlight as well.

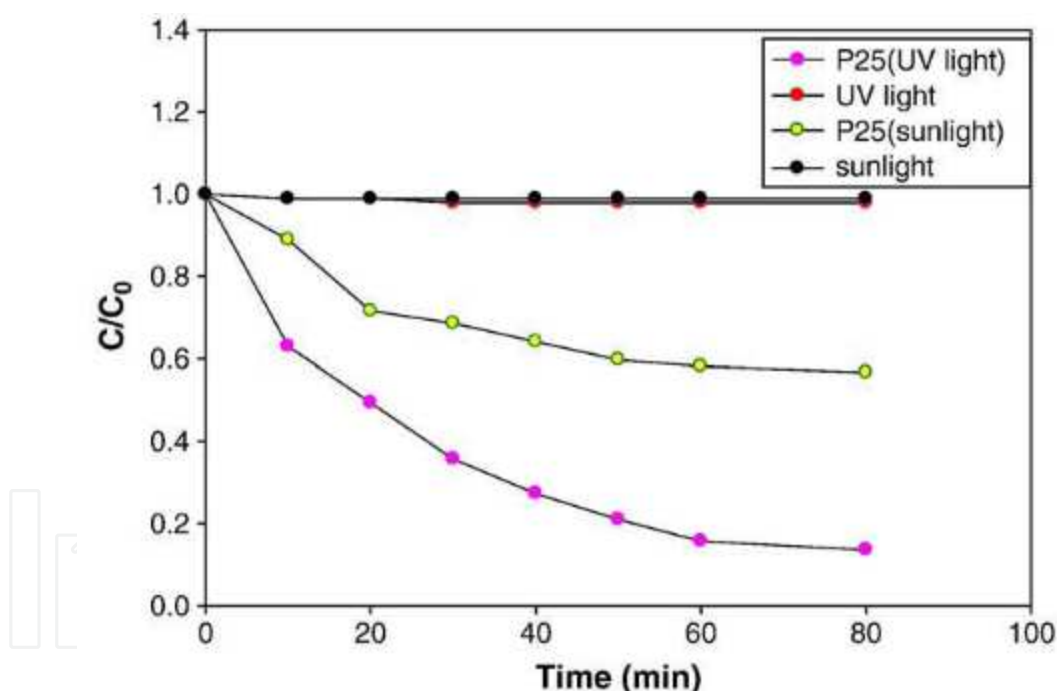


Fig. 14. Change in concentration on irradiation of an aqueous suspension in the presence and absence of  $\text{TiO}_2$  (Degussa P25,  $1\text{gL}^{-1}$ ) containing acetamiprid (0.1 mM), Light source: Pyrex filtered output of a medium pressure mercury lamp and sunlight.

### 3.8 Characterization of intermediate products

The identification and characterization of by-products formed during the photodegradation of organic pollutants has been of great interest among the people working in this area around the world. A brief summary showing the starting material and by-products under photolytic condition is shown below in Chart 2.

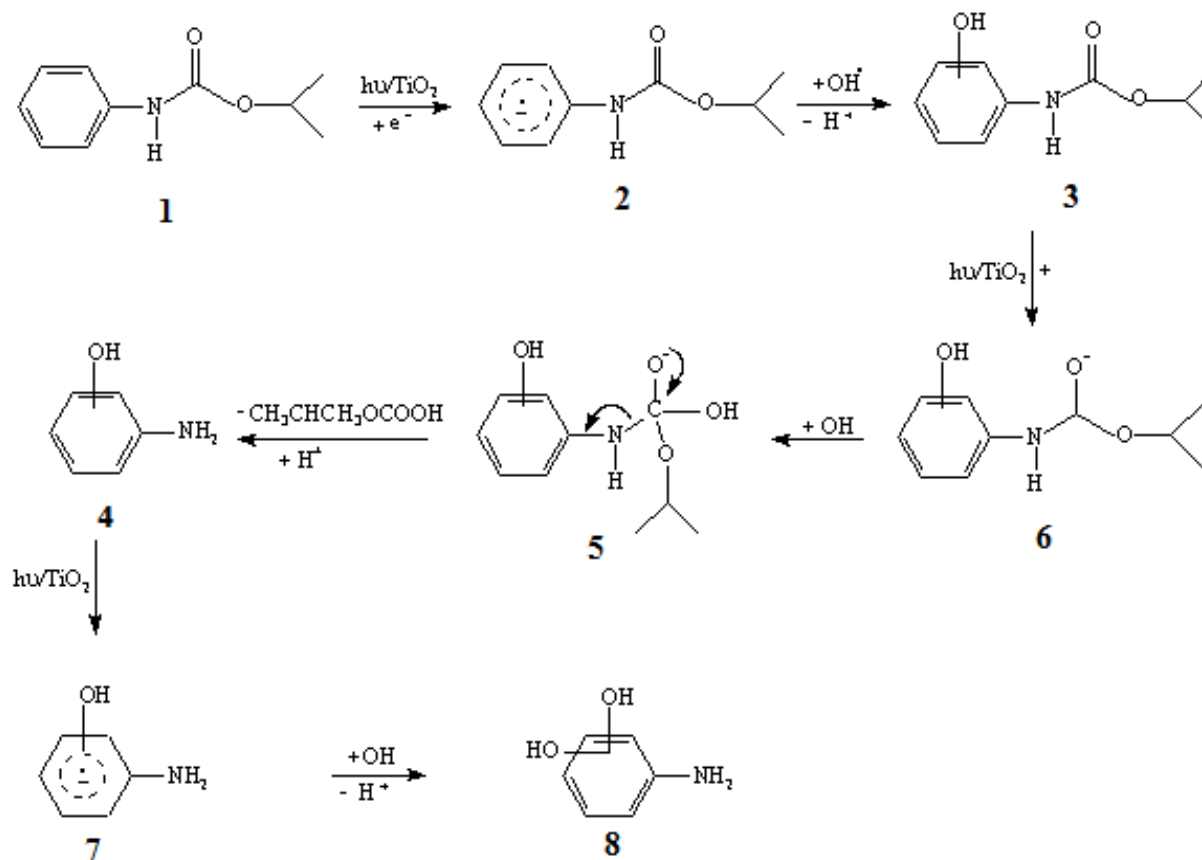
S. No.	Compound	By-products	Reference
1.	Pyridaben	Fragmented products	Zhu et al., 2004
2	Urea derivative	Hydroxylated, Phenyl Hydroxy Ureas, Aniline Derivatives	Lhomme et al., 2005; Vulliet et al., 2002; Maurino et al., 1999; Pramauro et al., 1993; Kinkennon et al., 1995; Richard & Bengana, 1996; Parra et al., 2000, 2002
3	Chlorophenols derivatives	Hydroxylated, Dechlorinated, Chloro Derivatives	Minero et al., 1996; Jardim et al., 1997; Tseng & Huang, 1991
4	Phenol	Catechol, Hydroquinone, 3-phenyl-2-propenal	Azevedo et al., 2009
5	Triazines derivative	Amido, Dealkylated, Hydroxylated, Ammeline, Cyanouric Acid	Goutailler et al., 2001; Konstantinou et al., 2001a; Pelizzetti et al., 1990, 1992a, 1992b; Minero et al., 1996; Muszkat et al., 1995; Sanlaville et al., 1996, Sleiman et al., 2006
6	Aniline and Amide derivative	Amines, Dechlorinated, Dealkylated, Cyclized, Aliphatics, Cyclized	Konstantinou et al., 2001b, 2002; Sakkas et al., 2004; Peñuela and Barceló, 1996; Pathirana & Maithreepala, 1997
7	Thiocarbamate derivative	Amine, Carboxy, Sulfoxide, Dealkylated	Vidal et al., 1999; Sturini et al., 1996; Vidal & Martin, 2001
8	Phenoxy-acids derivatives	Hydroxylated, Carboxylated, Chlorophenols, Quinonidal	Herrmann et al., 1998; Topalov et al., 2000; Barbeni et al., 1987; Poullos et al., 1998;
9	Organophosphorus derivatives	Hydroxy, Oxon, Phenol, Dialkylated, Trialkyl esters, Fragmented products	Herrmann, 1999; Konstantinou et al., 2001a, Oncescu et al., 2010; Herrmann et al., 1999; Hua et al., 1995; Sakkas et al., 2002; Dominguez et al., 1998
10	Carbamate derivative	Hydroxylated, Decarboxylated, Phenolic, Dealkylated, Cyclized	Tamimi et al., 2006; Percerancier et al., 1995; Pramauro et al., 1997; Tanaka et al., 1999; Marinas et al., 2001; Bianco Prevot et al., 1999;
11	Organochlorine derivative	Hydroxy, Dechlorinated	Guillard et al., 1996; Vidal, 1998; Zalenska et al., 2000; Peñuela & Barceló, 1998a, 1998b; Pichat 1997
12	Pyridines	Fragmented, Hydroxylated	Stapleton et al., 2010

Chart 2.

We have also made an attempt to identify the intermediate products formed in the photocatalytic degradation of variety of pesticide derivatives in aqueous suspensions of titanium dioxide through GC-MS analysis technique. Results on the photocatalytic degradation of few selected pesticide derivatives for product analysis are shown below;

### 3.8.1 Photocatalysis of propham (1)

Irradiation of an aqueous solution of propham (1) in the presence of Degussa P25  $\text{TiO}_2$  and analysis of the irradiated mixture at different time intervals through GC-MS analysis showed the formation of several intermediate products out of which, two products appearing at retention times ( $t_R$ ) 12.95 and 14.81 min., respectively were characterized as products 3 and 8, on the basis of molecular ion and fragmentation pattern (Muneer et al., 2005). A probable mechanism for the formation of these products from propham (1) involving electron transfer reactions and reactions with hydroxyl radical and superoxide radical anions formed in photocatalytic system, is shown in Scheme 1. The model compound 1, upon the transfer of an electron can form the radical anion 2, which may undergo addition of a hydroxyl radical either at ortho or para position followed by loss of a proton to give the observed product 3. This compound on further transfer of an electron followed by addition of a hydroxyl group can undergo cleavage reaction to give 4. This intermediate on subsequent transfer of an electron can undergo addition of a hydroxyl group to give the observed product 8.

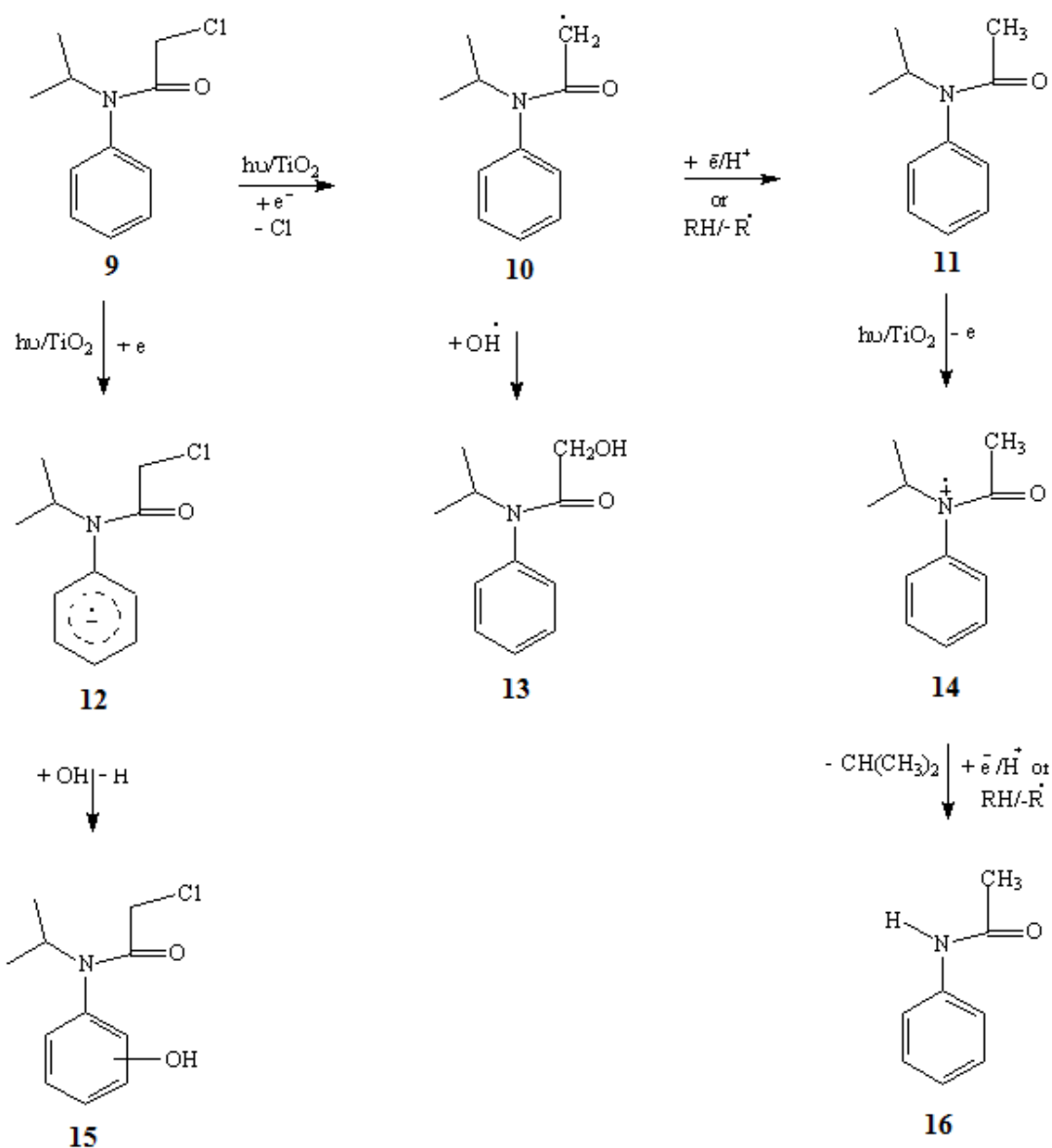


Scheme 1.



### 3.8.2 Photocatalysis of propachlor (9)

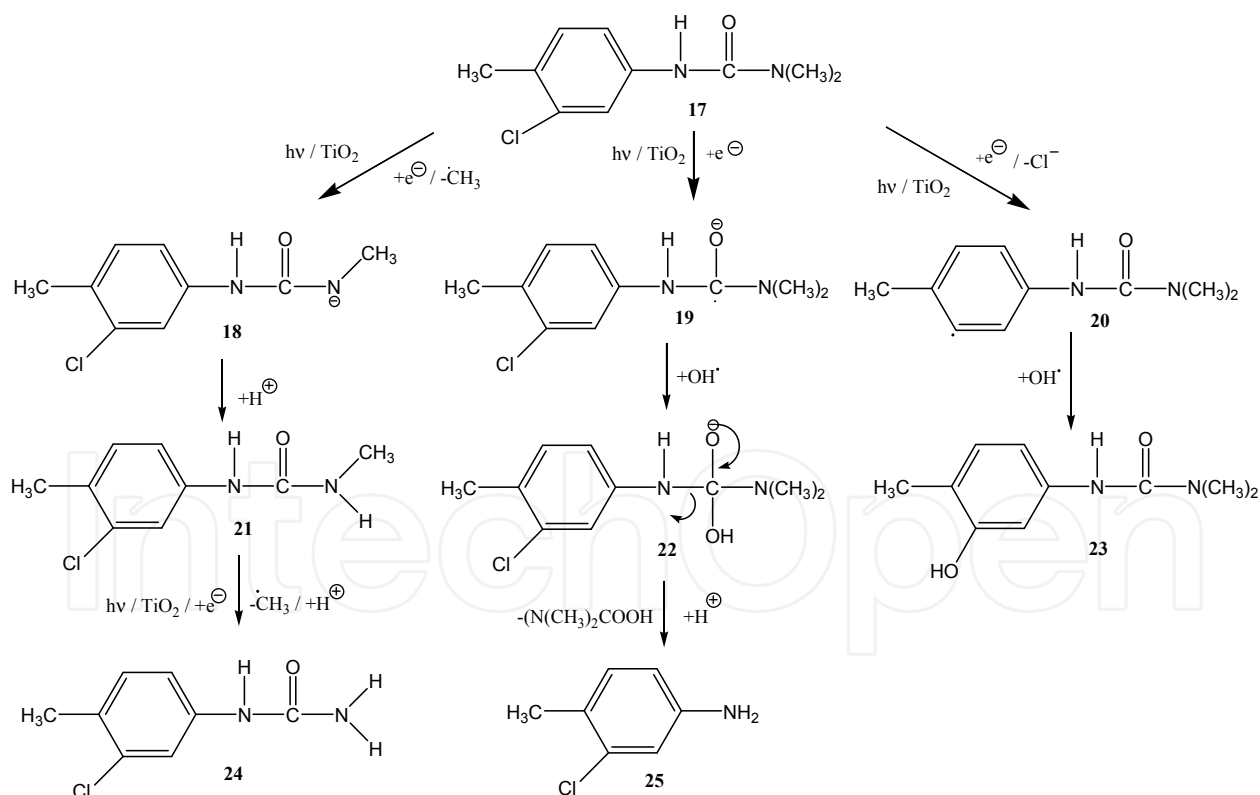
The GC-MS analysis of an irradiated mixture of propachlor (9) in the presence of  $\text{TiO}_2$  showed the formation of several by-products. A plausible mechanism for the formation of the different products such as N-Isopropyl-N-phenyl-acetamide (11), 2-Hydroxy-N-isopropyl-N-phenyl acetamide (13), hydroxyl inserted product (15) and N-phenyl-acetamide (16) from propachlor (9) involving similar reactive species, is proposed in Scheme 2 (Muneer et al., 2005). The model compound, 9 on transfer of an electron can form the radical species 10 on removal of chloride ion. This radical species can lead to the observed products 11 and 13, on abstraction of a hydrogen atom or hydroxyl radical. The product 11, on further transfer of an electron can form the radical species 14, which may lose isopropyl to give the observed product 16. The formation of 15 could be understood in terms of pathways shown in Scheme 2 through electron transfer to give radical anion species 12 followed by addition of hydroxyl radical.



Scheme 2.

### 3.8.3 Photocatalysis of chlorotoluron (17)

The steady state photolysis of an aqueous suspension of chlorotoluron (17) in the presence of  $\text{TiO}_2$  under constant bubbling of atmospheric oxygen for 2 h showed the formation of several products, of which, three products such as 3-(3-Hydroxy-4-methylphenyl)-1,1-dimethylurea (23) (3-chloro-4-methylphenyl) urea (24) and 3-chloro-4-methylphenylamine (25) appearing at retention times ( $t_R$ ) 10.310 min, 10.255 min and 5.520 min., respectively were identified on the basis of molecular ion and fragmentation pattern with those reported in the GC/MS NIST library, along with some unchanged starting material (17) appearing at ( $t_R$ ) 5.097 min. (Haque et al., 2006). A possible mechanism for the formation of products 23, 24 and 25 from chlorotoluron (17) involving electron transfer reaction and reaction with hydroxyl radicals could be understood in terms of pathways as shown in Scheme 3. The model compound 17, upon the transfer of an electron followed by the loss of methyl radical and abstraction of a proton to give species 21. This species on subsequent similar reaction can give the observed product 24. The observed product 25 from 17 may be arising through the transfer of an electron to give radical anionic species 19, which may undergo addition of a hydroxyl radical to give 22. This species may lose  $\text{N}(\text{CH}_3)_2\text{COOH}$  followed by abstraction of a proton to give the observed product 25 as shown in the Scheme 3. The product 23 could be formed upon the transfer of an electron followed by the loss of chloride ion with subsequent addition of hydroxyl radical as shown in scheme below.

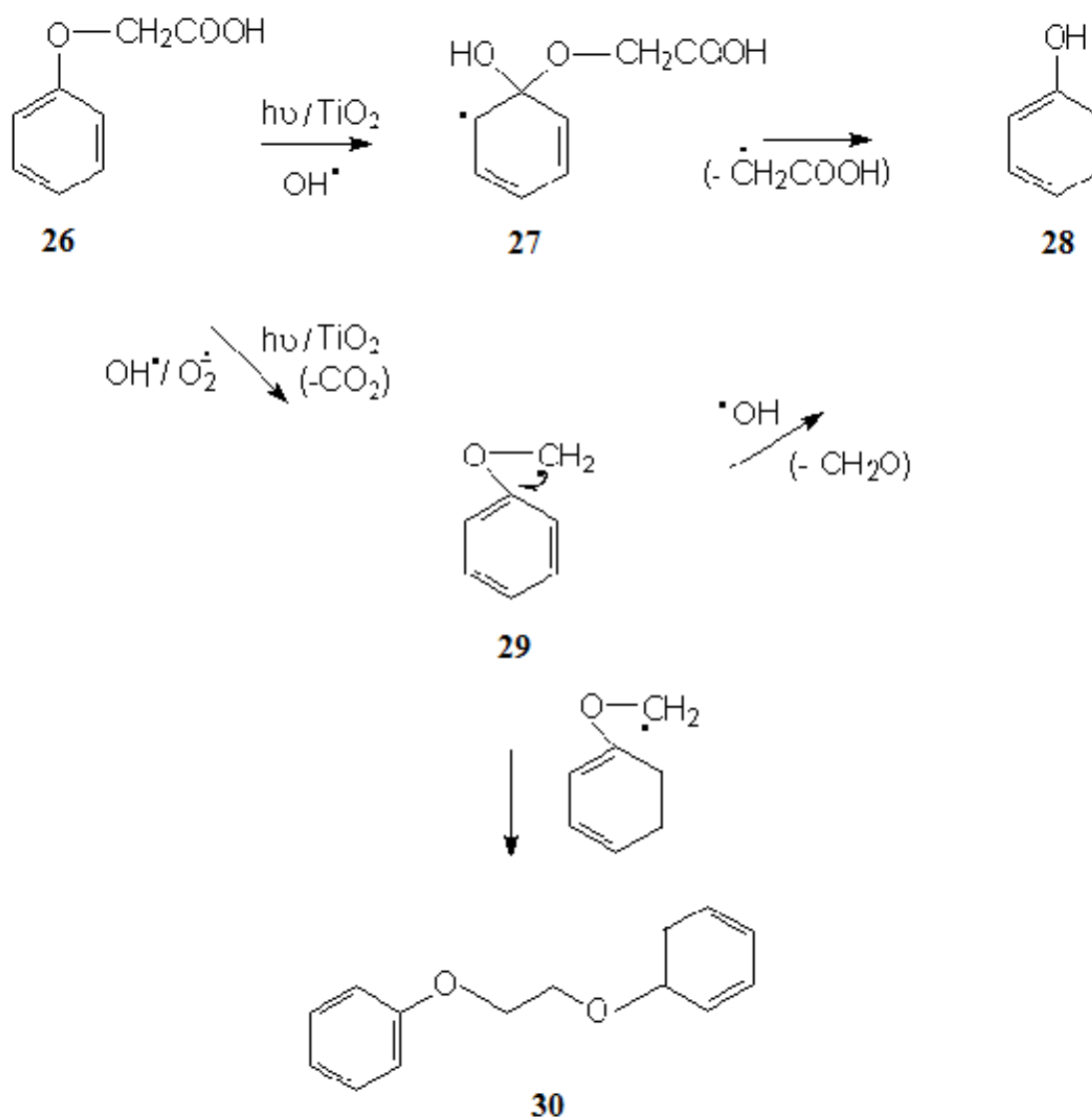


Scheme 3.

### 3.8.4 Photocatalysis of phenoxyacetic acid (26)

The desired concentration of an aqueous solution of phenoxyacetic acid (26) was irradiated in the presence of Degussa P25 and the analysis of the reaction mixture under analogous

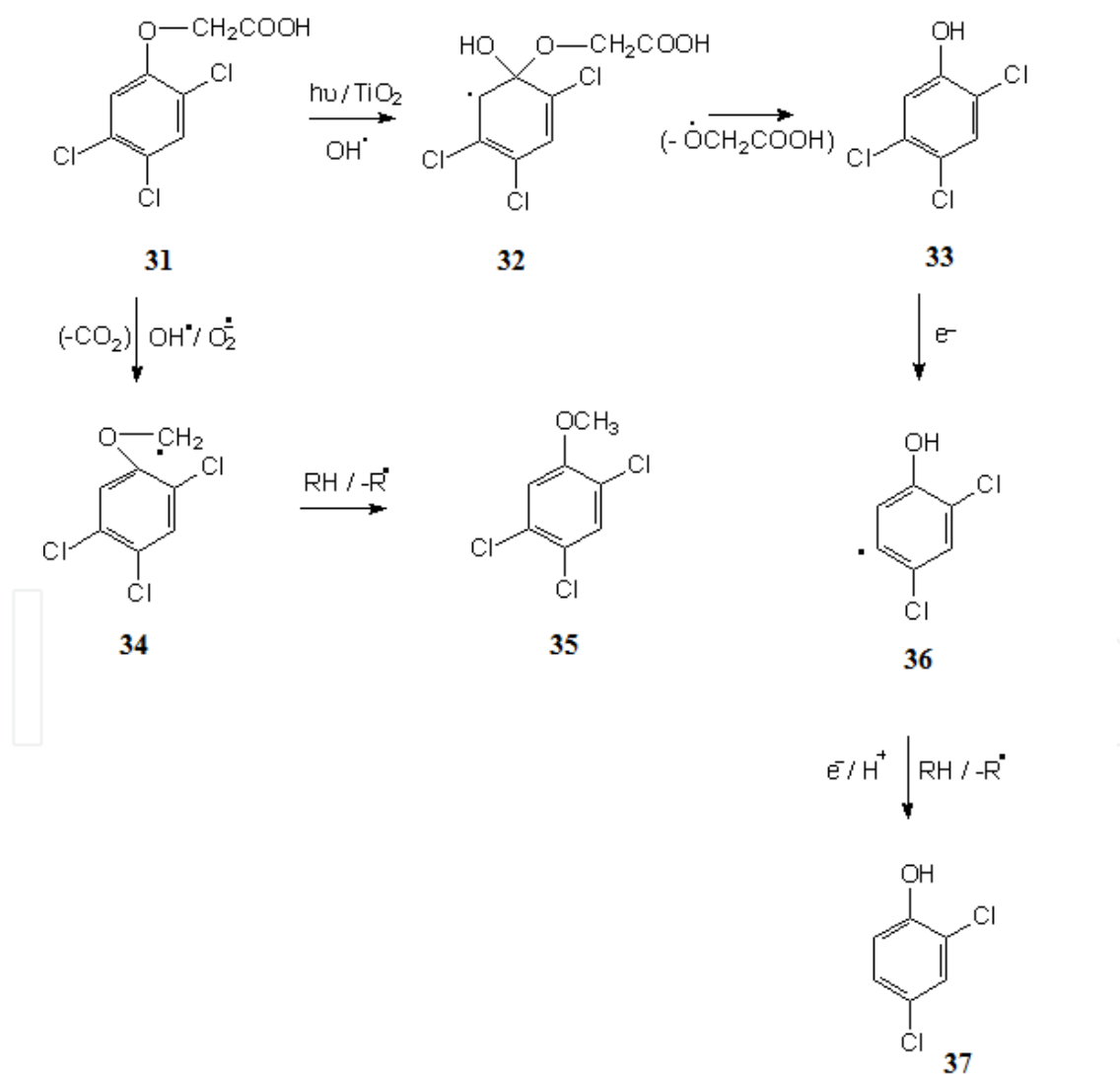
conditions, showed the formation of several intermediate products of which two intermediate products phenol (28) and 1,2-diphenoxyethane (30) appearing at retention time ( $t_R$ ) 2.92 and 9.84 min., respectively (Singh et al., 2007a). These products were identified by comparing its molecular ion and mass fragmentation peaks with those reported in the NIST library. A plausible mechanism for the formation of these products involving reactions with hydroxyl radical and superoxide radical anion formed in the photocatalytic process is shown in Scheme 4. The model compound undergoes addition of a hydroxyl radical leading to the formation of a radical species 27, which may undergo loss of ( $\cdot\text{OCH}_2\text{COOH}$ ) to give the observed product phenol (28). Alternatively, the model compound 26 on addition of hydroxyl radical followed by loss of  $\text{CO}_2$  may lead to the formation of the radical species 29. This species can either lose formaldehyde molecule followed by addition of hydroxyl radical led to the formation of phenol or can combine with another radical species leading to the formation of the 1,2-diphenoxyethane (30).



Scheme 4.

### 3.8.5 Photocatalysis of 2,4,5-trichlorophenoxy acetic acid (31)

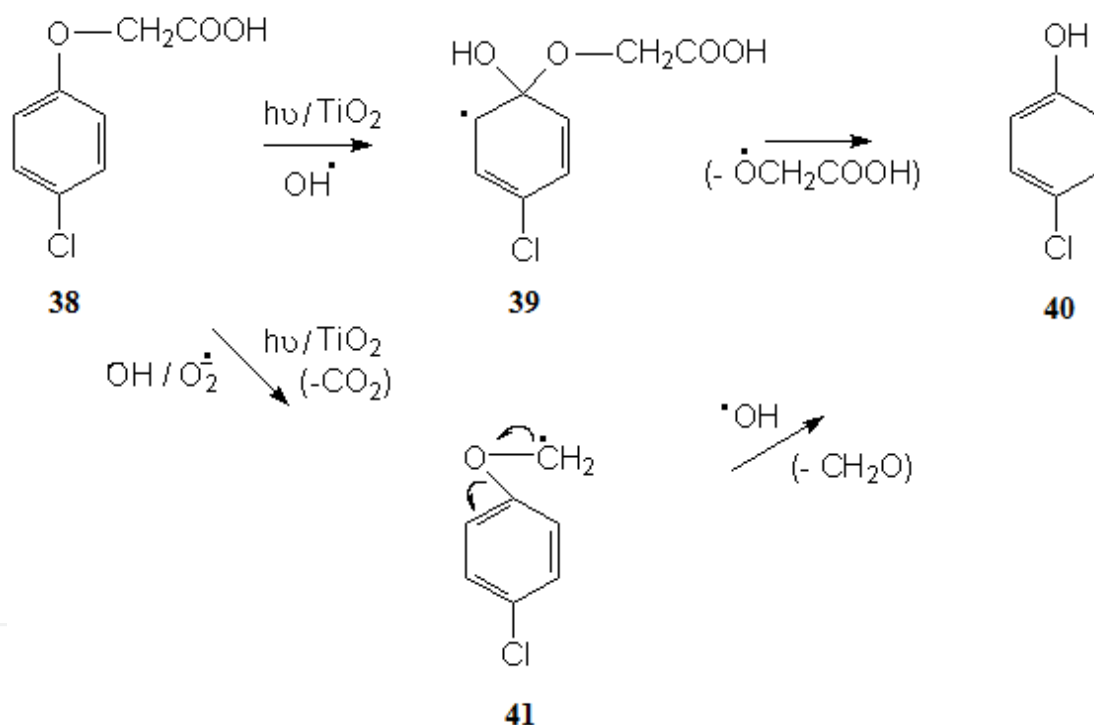
Analysis of the irradiated aqueous mixture of 2,4,5-trichlorophenoxy acetic acid (31) in the presence of photocatalyst showed the formation of three intermediate products namely, 2,4,5-trichlorophenol (33), 2,4-dichlorophenol (37) and 1,2,4-trichloro-5-methoxy benzene (35) appearing at retention times 4.11, 6.3 and 12.86 min., respectively and were identified by comparing their molecular ion and mass fragmentation peaks with those reported in the NIST library (Singh et al., 2007a). The model compound 31 on addition of a hydroxyl radical can lead to the formation of a radical species 32, which may undergo loss of ( $\cdot\text{OCH}_2\text{COOH}$ ) group to give the observed product 2,4,5-trichlorophenol (33). Alternatively, the model compound 31 upon the transfer of an electron followed by loss of  $\text{CO}_2$  may lead to the formation of the radical species 34. This species abstracts a hydrogen atom to form the observed product 1,2,4-trichloro-5-methoxy benzene (35). The product, 33 on further transfer of an electron may undergo loss of chlorine atom followed hydrogen atom abstraction giving 2,4-dichlorophenol (37) as shown in Scheme 5.



Scheme 5.

### 3.8.6 Photocatalysis of 4-chlorophenoxy acetic acid (38)

Irradiation of 4-chlorophenoxyacetic acid (4-CPA, 38) in the presence of titanium dioxide showed the formation of 4-chlorophenol (40), which was identified by comparing its molecular ion and fragment ion peak with those reported in the NIST library (Singh et al., 2007b). A plausible mechanism for the formation of product, 40 involving reactions with hydroxyl radicals formed in the photocatalytic process is shown in Scheme 6. The model compound, 4-CPA undergoes addition of a hydroxyl radical formed in the photocatalytic process leading to the formation of a radical species 39 as an intermediate, which may undergo loss of ( $\cdot\text{OCH}_2\text{COOH}$ ) group to give the observed product 4-chlorophenol (40). Alternatively, the model compound 4-CPA (38) on addition of hydroxyl radical followed by loss of  $\text{CO}_2$  may lead to the formation of the intermediate radical species 41, which upon loss of formaldehyde molecule followed by addition of hydroxyl radical led to the formation of the observed product 4-chlorophenol (40).



Scheme 6.

## 4. Conclusions

The results of these studies clearly indicate that  $\text{TiO}_2$  can efficiently catalyse the photodegradation and photomineralization of the pollutants in the presence of light and oxygen. In most of the cases the photocatalyst Degussa P25 was found to be more efficient as compare to other photocatalyst  $\text{TiO}_2$  powders. But in few cases Hombikat UV100 has also found to be more efficient photocatalyst. The addition of electron acceptor enhanced the degradation rate of the pollutants. The results also indicate that degradation rates could be influenced not only by the different parameters such as type of photocatalyst, catalyst concentration, substrate concentration, pH and additives and their concentration but also by

the model pollutants. The observations of these investigations clearly demonstrate the importance of choosing the optimum degradation parameters to obtain high degradation rate, which is essential for any practical application of photocatalytic oxidation processes. The intermediate products formed during the process are also a useful source of information for the degradation pathways.

## 5. Acknowledgements

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## 6. References

- Augustynski, J. (1988) In: *Structural Bonding*, Springer, Berlin, New York, p. 69 (Chapter1).
- Azevedo, E.B., Tôrres, A.R., Aquino Neto, F.R., & Dezotti, M., (2009). TiO<sub>2</sub>-Photocatalyzed degradation of phenol in saline media in an annular reactor: hydrodynamics, lumped kinetics, intermediates, and acute toxicity. *Brazilian J. Chem. Engg.*, 26, 75 – 87.
- Bahnemann, W., Muneer, M., & Haque, M.M., (2007). Titanium dioxide-mediated photocatalysed degradation of few selected organic pollutants in aqueous suspensions. *Catal. Today*, 124, 133-148.
- Barbeni, M., Morello, M., Pramauro, E., & Pelizzetti, E., (1987). Sunlight photodegradation of 2,4,5-trichlorophenoxy-acetic acid and 2,4,5, trichlorophenol on TiO<sub>2</sub>. Identification of intermediates and degradation pathway. *Chemosphere*, 16, 1165-1179.
- Barni, B., Cavicchioli, A., Riva, E., Zaroni, L., Bignoli, F., Bellobono, I.R., Gianturco, F., De Giorgi, A., Muntau, H., Montanarella, L., Facchetti, S., & Castellano, L., (1995). Pilot-plant-scale photodegradation of phenol in aqueous solution by photocatalytic membranes immobilizing titanium dioxide (PHOTOPERM® process). *Chemosphere*, 30, 1861-1874.
- Bellobono, I.R., Carrara, A., Barni, B., & Gazzotti, A., (1994). Laboratory- and pilot-plant-scale photodegradation of chloroaliphatics in aqueous solution by photocatalytic membranes immobilizing titanium dioxide. *J. Photochem. Photobiol. A:Chem.*, 84, 83-90.
- Berry, R.J., & Mueller, M.R., (1994). Photocatalytic decomposition of crude oil slicks using TiO<sub>2</sub> on a floating substrate. *Microchem. J.*, 50, 28-32.
- Bianco Prevot, A., Pramauro, E., & de la Guardia, M., (1999). Photocatalytic degradation of carbaryl in aqueous TiO<sub>2</sub> suspensions containing surfactants. *Chemosphere*, 39, 493-502.
- Blake, D. M. (2001). Bibliography of work on the photocatalytic Removal of Hazardous Compounds from Water and Air, National Renewal Energy Laboratory, USA.
- Blanco, J., Avila, P., Bahamonde, A., Alvarez, E., Sanchez, B., & Romero, M., (1996). Photocatalytic destruction of Toluene and Xylene at gas-phase on a titania based monolithic catalyst. *Catal Today*, 29, 437-442.



- Bravo, A., Garcia, J., Domenech, X., & Peral, J., (1994). Some observations about the photocatalytic oxidation of cyanate to nitrate over  $\text{TiO}_2$ . *Electrochim. Acta*, 39, 2461-2463.
- Byrne, J.A., Davidson, A., Dunlop, P.S.M., & Eggins, B.R., (2002). Water treatment using nano-crystalline  $\text{TiO}_2$  electrodes. *J. Photochem. Photobiol. A:Chem.*, 148, 365-374.
- Cohen, Z.Z., Eiden, C., Lober, M.N., (1986). In: Gerner, W.Y., (Ed.), *Evaluation of Pesticide in Ground Water*, ACS Symposium Series 315, American Chemical Society, Washington, DC, p. 170.
- Daneshvar, N., Salari, D., & Khataee, A.R., (2004). Photocatalytic degradation of azo dye acid red 14 in water on  $\text{ZnO}$  as an alternative catalyst to  $\text{TiO}_2$ . *J. Photochem. Photobiol. A Chem.*, 162, 317-322.
- Dominguez, C., Garcia, J., Pedraz, M.A., Torres, A., & Galan, M.A., (1998). Photocatalytic oxidation of organic pollutants in water. *Catal. Today*, 40, 85-101.
- Dowd, R. M., Anderson, M. P., & Johnson, M. L. (1998). Proceedings of the Second National Outdoor Action Conference on Aquifer Restoration, Groundwater Monitoring Geophysical Methods, National Water Well Association, Dublin, OH, p. 1365.
- Draper, R.B., & Fox, M.A., (1990). Titanium dioxide photooxidation of thiocyanate:  $(\text{SCN})_2$  studied by diffuse reflectance flash photolysis. *J. Phys. Chem.*, 94, 4628-4634.
- Dunlop, P.S.M., Byrne, J.A., Manga, N., & Eggins, B.R., (2002). The photocatalytic removal of bacterial pollutants from drinking water. *J. Photochem. Photobiol. A:Chem.*, 148, 355-363.
- Evgenidou, E., Bizani, E., Christophoridis, C., & Fytianos, K. (2007). Heterogeneous photocatalytic degradation of prometryn in aqueous solutions under UV/Vis irradiation. *Chemosphere*, 68, 1877-1882.
- Frank, S.N., & Bard, A.J., (1977). Heterogeneous photocatalytic oxidation of cyanide and sulfite in aqueous solutions at semiconductor powders. *J. Phys. Chem.*, 81, 1484-1488.
- Fujishima, A., & Honda, K., (1972). Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature*, 238, 37-38.
- Funazaki, N., Hemmi, A., Ito, S., Asano, Y., Yano, Y., Miura, N., & Yamazoe, N., (1995). Application of semiconductor gas sensor to quality control of meat freshness in food industry. *Sensors & Actuators, B* 24-25, 797-800.
- Garcia, J.C., & Takashima, K. (2003). Photocatalytic degradation of imazaquin in an aqueous suspension of titanium dioxide. *J. Photochem. Photobiol. A: Chem.*, 155, 215-222.
- Gaya, U.I., & Abdullah, A.H., (2008). Heterogeneous photocatalytic degradation of organic contaminants over titanium dioxide: A review of fundamentals, progress and problems. *J. Photochem. Photobiol. C: Photochem. Rev.*, 9, 1-12.
- Gerisher, H., & Heller, A., (1992). Photocatalytic oxidation of organic molecules at  $\text{TiO}_2$  particles by sunlight in aerated water. *J. Electrochem. Soc.*, 139, 113-118.
- Gianturco, F., Chiodaroli, C.M., Bellobono, I.R., Raimondi, M.L., Moroni, A., & Gawlik, B., (1997). Pilot-plant photomineralization of atrazine in aqueous solution by photocatalytic membranes immobilising titanium dioxide and promoting photocatalysts. *Fresenius Environ. Bull.*, 6, 461-468.

- Goutailler, G., Valette, J.C., Guillard, C., Paissé, O., & Faure, R., (2001). Photocatalysed degradation of cyromazine in aqueous titanium dioxide suspensions: comparison with photolysis. *J. Photochem. Photobiol. A: Chem.*, 141, 79-84.
- Grätzel, M., (1981). Artificial photosynthesis: water cleavage into hydrogen and oxygen by visible light. *Acc. Chem. Res.*, 14, 376-384.
- Guillard, C., Pichat, P., Huber, G., & Hoang-Van, C., (1996). The GC-MS analysis of organic intermediates from the TiO<sub>2</sub> photocatalytic treatment of water contaminated by Lindane (1 $\alpha$ ,2 $\alpha$ ,3 $\beta$ ,4 $\alpha$ ,5 $\alpha$ ,6 $\beta$ , hexachlorocyclohexane). *J. Adv. Oxid. Technol.*, 1, 53-60.
- Gupta, H., & Tanaka, S., (1995). Photocatalytic Mineralisation of Perchloroethylene Using Titanium Dioxide. *Wat. Sci. Technol.*, 31, 47-54.
- Hallam, M. (1992). Photodegradation of di-n-butyl-ortho-phthalate in aqueous solution. *J. Photochem. Photobiol. A: Chem.*, 66, 215-223.
- Halmann, M.M., (1996). *Photodegradation of Water Pollutants*, CRC Press Inc, Boca Raton, Florida
- Haque, M.M., & Muneer, M., (2003). Heterogeneous photocatalysed degradation of a herbicide derivative, isoproturon in aqueous suspension of titanium dioxide. *J. Environ. Manag.*, 69, 169-176.
- Haque, M.M., Muneer, M., & Bahnemann, D., (2006). Semiconductor-Mediated photocatalysed degradation of a herbicide derivative, chlorotoluron, in aqueous suspensions. *Environ. Sci. Technol.*, 40, 4765-4770.
- Herrmann, J.M., (1999). Heterogeneous photocatalysis: fundamentals and applications to the removal of various types of aqueous pollutants. *Catal. Today*, 53, 115-129.
- Herrmann, J.M., Disdier, P., Pichat, P., Malato, S., & Blanco, J., (1998). TiO<sub>2</sub>-based solar photocatalytic detoxification of water organic pollutants. Case studies of 2,4-dichlorophenoxyacetic acid (2,4-D) and of benzofuran. *J. Appl. Catal. B: Environ.*, 17, 15-23.
- Herrmann, J.M., Guillard, C., Arguello, M., Agüera, A., Tejedor, A., Piedra, L., & Fernández-Alba, A., (1999). Photocatalytic degradation of pesticide pirimiphos-methyl: Determination of the reaction pathway and identification of intermediate products by various analytical methods. *Catal. Today*, 54, 353-367.
- Hua, Z., Manping, Z., Zongfeng, X., & Low, G.K.C., (1995). Titanium dioxide mediated photocatalytic degradation of monocrotophos. *Water Res.* 29, 2681-2688.
- Huang, I.W., Hong, C.S., & Bush, B., (1996). Photocatalytic degradation of PCBs in TiO<sub>2</sub> aqueous suspensions. *Chemosphere*, 32, 1869-1881.
- Hurum, D.C., Agrios, A.G., Gray, K.A., Rajh T., & Thurnauer, M.C., (2003). Explaining the enhanced photocatalytic activity of Degussa P25 mixed-phase TiO<sub>2</sub> using EPR. *J. Phy. Chem. B*, 107, 4545-4549.
- Irvine, J.T.S., Eggins, B.R., & Grimshaw, J., (1990). Solar energy fixation of carbon dioxide via cadmium sulphide and other semiconductor photocatalysts. *J. Sol. Energy*, 45, 27-33.
- Jardim, W.F., Moraes, S.G., & Takiyama, M.M.K., (1997). Photocatalytic degradation of aromatic chlorinated compounds using TiO<sub>2</sub>: toxicity of intermediates. *Water Res.* 31, 1728-1732.

- Khan, A., Haque, M.M., Mir, N.A., Muneer, M., & Boxall, C. (2010). Heterogeneous photocatalysed degradation of an insecticide derivative acetamiprid in aqueous suspensions of semiconductor. *Desalination*, 261, 169-174.
- Khan, M.M.T., & Rao, N.N., (1991). Stepwise reduction of coordinated dinitrogen to ammonia via diazinido and hydrazido intermediates on a visible light irradiated Pt/CdS · Ag<sub>2</sub>S/RuO<sub>2</sub> particulate system suspended in an aqueous solution of K[Ru(EDTA-H)Cl]2H<sub>2</sub>O. *J. Photochem. Photobiol. A: Chem.*, 56, 101-111.
- Kinkennon, A.E., Green, D.B., & Hutchinson, B., (1995). The use of simulated or concentrated natural solar radiation for the TiO<sub>2</sub>-mediated photodecomposition of basagran, diquat, and diuron. *Chemosphere*, 31, 3663-3671.
- Konstantinou, I.K., Sakellarides, T.M., Sakkas, V.A., & Albanis, T.A., (2001a). Photocatalytic Degradation of Selected s-Triazine Herbicides and Organophosphorus Insecticides over Aqueous TiO<sub>2</sub> Suspensions. *Environ. Sci. Technol.* 35, 398-405.
- Konstantinou, I.K., Sakkas, V.A., & Albanis, T.A., (2001b). Photocatalytic degradation of the herbicides propanil and molinate over aqueous TiO<sub>2</sub> suspensions: identification of intermediates and the reaction pathway. *Appl. Catal. B: Environ.*, 34, 227-239.
- Konstantinou, I.K., Sakkas, V.A., & Albanis, T.A., (2002). Photocatalytic degradation of propachlor in aqueous TiO<sub>2</sub> suspensions. Determination of the reaction pathway and identification of intermediate products by various analytical methods. *Wat. Res.*, 36, 2733-2742.
- Kosanac, M.M., & Topalov, A.S., (1990). Photochemical hydrogen production from CdS/RhOx/Na<sub>2</sub>S dispersions. *Int. J. Hydrogen Energy*, 15, 319-323.
- Krosley, K.W., Collard, D.M., Adamson, J., Fox, M.A., (1993). Degradation of organophosphonic acids catalyzed by irradiated titanium dioxide. *J. Photochem. Photobiol. A:Chem.*, 69, 357-360.
- Kubota, Y., Shuin, T., Kawasaki, C., Hosaka, M., Kitamura, H., Cai, R., Sakai, H., Hashimoto, K., & Fujishima, A., (1994). Photokilling of T-24 human bladder cancer cells with titanium dioxide. *British J. Cancer*, 70, 1107-1111.
- Lee, S., Nishida, K., Otaki, M., & Ohgaki, S., (1997). Photocatalytic inactivation of phage Q $\phi$  by immobilized titanium dioxide mediated photocatalyst. *Wat. Sci. Technol.*, 35, 101-106.
- Legrini, O., Oliveros, E., & Braun, A.M., (1993). Photochemical processes for water treatment. *Chem Rev.*, 93, 671-698.
- Lhomme, L., Brosillon, S., Wolbert, D., & Dussaud, J., (2005). Photocatalytic degradation of a phenylurea, chlortoluron, in water using an industrial titanium dioxide coated media. *Appl. Catal B: Environ.*, 61, 227- 235.
- Linder, M., (1997) Ph.D. Thesis, Department of Chemistry, University of Hannover, Hannover, Germany.
- Lindner, M., Bahnemann, D., Hirthe, B., & Griebler, W.D. (1995). *Novel TiO<sub>2</sub> powders as highly active photocatalysts. In Solar Water Detoxification; Solar Engineering*, Stine, W. B., Tanaka, T., Claridge, D.E., Eds.; ASME: New York, 339.
- Liu, I., Lawson, L.A., Cornish, B., & Robertson, P.K.J., (2002). Mechanistic and toxicity studies of the photocatalytic oxidation of microcystin-LR. *J. Photochem. Photobiol. A:Chem.*, 148, 349-354.

- Lobedank, J., Bellmann, E., & Bendig, J., (1997). Sensitized photocatalytic oxidation of herbicides using natural sunlight. *J. Photochem. Photobiol. A:Chem.*, 108, 89-93.
- Lu, M.C., Roam, G.D., Chen, J.N., & Huang, C.P., (1995). Photocatalytic mineralization of toxic chemicals with illuminated TiO<sub>2</sub>. *Chem. Eng. Commun.*, 139, 1-13.
- Mao, Y., & Bakac, A. (1996). Photocatalytic Oxidation of Aromatic Hydrocarbons. *Inorg. Chem.*, 35, 3925-3930.
- Marinas, A., Guillard, C., Marinas, J.M., Fernández-Alba, A., Agüera, A., & Herrmann, J.M., (2001). Photocatalytic degradation of pesticide-acaricide formetanate in aqueous suspension of TiO<sub>2</sub>. *Appl. Catal. B: Environ.*, 34, 241-252.
- Martin, C.A., Baltanas, M.A., Cassano, A.E., (1994). Photocatalytic reactors.3. kinetics of the decomposition of chloroform including effects. *Environ. Sci. Technol.*, 30, 2355-2364.
- Matsunaga, T., & Okochi, M., (1995). TiO<sub>2</sub>-Mediated Photochemical Disinfection of Escherichia coli Using Optical Fibers. *Environ. Sci. Technol.*, 29, 501-505.
- Maurino, V., Minero, C., Pelizzetti, E., & Vincenti, M., (1999). Photocatalytic transformation of sulfonylurea herbicides over irradiated titanium dioxide particles. *Coll.Surf. A* 151, 329-338.
- Mihaylov, B.V., Hendrix, J.L., & Nelson, J.H., (1993). Comparative catalytic activity of selected metal oxides and sulphides for the photo-oxidation of cyanide. *J. Photochem. Photobiol. A:Chem.*, 72, 173-177.
- Mills, A., & Le Hunte, S. (1997). An overview of semiconductor photocatalysis. *J. Photochem. Photobiol. A:Chem.*, 108, 1-35.
- Mills, A., Belghazi, A., & Rodman, D., (1996). Bromate removal from drinking water by semiconductor photocatalysis. *Wat. Res.*, 30, 1973-1978.
- Mills, A., Peral, J., Domenech, X., & Navio, J.A., (1994). Heterogeneous photocatalytic oxidation of nitrite over iron-doped TiO<sub>2</sub> samples. *J. Mol. Catal.*, 87, 67-74.
- Minero, C., Pelizzetti, E., Malato, S., & Blanco, J. (1996). Large solar plant photocatalytic water decontamination: degradation of atrazine. *Solar Energy*, 56, 411-419.
- Muneer, M., & Bahnemann, D., (2001). Semiconductor mediated photocatalysed degradation of two selected pesticide derivatives, terbacil and 2,4,5-tribromoimidazole in aqueous suspension. *Water Sci. Technol.*, 144, 331-337.
- Muneer, M., & Bahnemann, D., (2002). Semiconductor mediated photocatalysed degradation of two selected pesticide derivatives, terbacil and 2,4,5-tribromoimidazole in aqueous suspension. *Appl. Catal. B: Environ.*, 36, 95-111.
- Muneer, M., Qamar, M., Saquib, M., & Bahnemann, D. (2005). Heterogeneous photocatalysed reaction of three selected pesticide derivatives, protham, propachlor and tebuthiuron in aqueous suspension of titanium dioxide. *Chemosphere*, 61, 457-468.
- Muneer, M., Singh, H.K., & Bahnemann, D., (2002). Photocatalysed degradation of two selected priority organic pollutants, benzidine and 1,2-diphenyl hydrazine in aqueous suspensions of titanium dioxide. *Chemosphere*, 49, 193-203.
- Muszkat, L., Bir, L., & Feigelson, L., (1995). Solar photocatalytic mineralization of pesticides in polluted waters. *J. Photochem. Photobiol. A: Chem.* 87, 85-88.
- Muszkat, L., Raucher, D., Magaritz, M., Ronen, D., (1994). In: Zoller, U., (Ed.), *Groundwater Contamination and Control*, Marcel Dekker, p.257.



- Nevim, S., Arzu, H., Gulin K., & Cinar, Z., (2001). Prediction of primary intermediates and the photodegradation kinetics of 3-aminophenol in aqueous TiO<sub>2</sub> suspensions. *J. Photochem. Photobiol. A: Chem.*, 139, 225-232.
- Nozik, A. J. in : Ollis, D. F., & EL-Ekabi, H., (Eds.), (1993). *Photocatalytic Purification and Treatment of water and Air*, Elsevier, Amsterdam, p. 391.
- O'Shea, K.E., Garcia, I., & Aguilar, M., (1997). TiO<sub>2</sub> Photocatalytic degradation of dimethyl- and diethyl-methylphosphonate, effects of catalyst and environmental factors. *Res. Chem. Intermed.*, 23, 325-339.
- Ohtani, B., Zhang, S.W., Nishimoto, S., & Kagiya, T., (1992). Catalytic and photocatalytic decomposition of ozone at room temperature over titanium(IV) oxide. *J. Chem. Soc. Faraday Trans.*, 88, 1049-1053.
- Oncescu, T., Stefan, M.I., & Oancea, P., (2010). Photocatalytic degradation of dichlorvos in aqueous TiO<sub>2</sub> Suspensions. *Environ. Sci. Pollut. Res.*, 17, 1158-1166.
- Parra, S., Olivero, J., & Pulgarin, C., (2002). Relationships between physicochemical properties and photoreactivity of four biorecalcitrant phenylurea herbicides in aqueous TiO<sub>2</sub> suspension. *Appl. Catal. B: Environ.* 36, 75-85.
- Parra, S., Sarria, V., Malato, S., Péringer, P., & Pulgarin, C., (2000). Photochemical versus coupled photochemical-biological flow system for the treatment of two biorecalcitrant herbicides: metobromuron and isoproturon. *Appl. Catal. B: Environ.*, 27, 153-168.
- Pathirana, H.M.K.K., & Maithreepala, R.A., (1997). Photodegradation of 3,4-dichloropropionamide in aqueous TiO<sub>2</sub> suspensions. *J. Photochem. Photobiol. A: Chem.*, 102, 273-277.
- Pelizzetti, E., Carlin, V., Minero, C., & Pramauro, E., (1992a). Degradation pathways of atrazine under solar light and in the presence of TiO<sub>2</sub> colloidal particles. *Sci. Total Environ.*, 123/124, 161-169.
- Pelizzetti, E., Maurino, V., Minero, C., Carlin, V., Pramauro, E., Zerbinati, O., & Tosato, M.L., (1990). Degradation of atrazine and other S-triazine herbicides. *Environ. Sci. Technol.*, 24, 1559-1565.
- Pelizzetti, E., Minero, C., Carlin, V., Vincenti, M., & Pramauro, E., (1992b). Identification of photocatalytic degradation pathways of 2-Cl-s-triazine herbicides and detection of their decomposition intermediates. *Chemosphere*, 24, 891-910.
- Peñuela, G.A., & Barceló, D., (1996). Comparative degradation kinetics of alachlor in water by photocatalysis with FeCl<sub>3</sub> and photolysis, studied by solid-phase disk extraction followed by gas chromatographic techniques. *J. Chromatogr. A*, 754, 187-195.
- Peñuela, G.A., & Barceló, D., (1998a). Photodegradation and stability of chlorothalonil in water studied by solid-phase disk extraction, followed by gas chromatographic techniques. *J. Chromatogr. A* 823, 81.
- Peñuela, G.A., & Barceló, D., (1998b). Application of C<sub>18</sub> disks followed by gas chromatography techniques to degradation kinetics, stability and monitoring of endosulfan in water. *J. Chromatogr. A* 795, 93-104.
- Percerancier, J.P., Chapelon, R., & Pouyet, B., (1995). Semiconductor-sensitized photodegradation of pesticides in water: the case of carbetamide. *J. Photochem. Photobiol. A: Chem.*, 87, 261-266.

- Peyton, G.R., & Glaze, W.H. (1988). Destruction of pollutants in water with ozone in combination with ultraviolet radiation. 3. Photolysis of aqueous ozone. *Environ. Sci. Technol.*, 22, 761-767.
- Pichat, P., (1997). Photocatalytic degradation of aromatic and alicyclic pollutants in water: by-products, pathways and mechanisms. *Water Sci. Tech.* 35, 73-78.
- Pirkanniemi, K., & Sillanpää, M., (2002). Heterogeneous water phase catalysis as an environmental application: a review. *Chemosphere*, 48, 1047-1060.
- Pizarro, P., Guillard, C., Perol, N., & Herrmann, J.-M., (2005). Photocatalytic degradation of imazapyr in water: Comparison of activities of different supported and unsupported TiO<sub>2</sub>-based catalysts. *Catal. Today.*, 101, 211-218.
- Pleskov, Y.V., & Krotova, M.D., (1993). Photosplitting of water in a photoelectrolyser with solid polymer electrolyte. *Electrochim Acta*, 38, 107-109.
- Pollema, C.H., Hendrix, J.L., Milosavljevic, E.B., Solujic, L., & Nelson, J.H., (1992). Photocatalytic oxidation of cyanide to nitrate at TiO<sub>2</sub> particles. *J. Photochem. Photobiol. A. Chem.*, 66, 235-244.
- Poulios, I., Kositzi, M., & Kouras, A., (1998). Photocatalytic decomposition of triclopyr over aqueous semiconductor suspensions. *J. Photochem. Photobiol. A: Chem.*, 115, 175-183.
- Pramauero, E., Bianco Prevot, A., Vinceti, M., & Brizzolesi, G., (1997). Photocatalytic degradation of cabranyl in aqueous solutions containig TiO<sub>2</sub> Suspensions. *Environ. Sci. Technol.*, 31, 3126-3131.
- Pramauero, E., Vincenti, M., Augugliaro, V., & Palmisano, L., (1993). Photocatalytic degradation of monuron in aqueous TiO<sub>2</sub> dispersions. *Environ. Sci. Technol.*, 27, 1790-1795.
- Qamar, M., Saquib, M., & Muneer, M., (2005). TiO<sub>2</sub>-mediated photocatalysed degradation of two selected azo dye derivative chrysidine R and acid red 29 in aqueous suspension. *Desalination*, 186, 255-271.
- Rahman, M.A., & Muneer, M., (2005). Photocatalysed degradation of two selected pesticide derivatives, dichlorvos and phosphamidon in aqueous suspension of titanium dioxide. *Desalination*, 181, 161-172.
- Ranjit, K.T., Varadarajan, T.K., & Viswanathan, B., (1995). Photocatalytic reduction of nitrite and nitrate ions to ammonia on Ru/TiO<sub>2</sub> catalysts. *J. Photochem. Photobiol. A:Chem.*, 89, 67-68.
- Ranjit, K.T., Varadarajan, T.K., & Viswanathan, B., (1996). Photocatalytic reduction of dinitrogen to ammonia over noble-metal-loaded TiO<sub>2</sub>. *J. Photochem. Photobiol. A:Chem.*, 96, 181-185.
- Rao, N.N., & Dube, S., (1996). Photocatalytic degradation of mixed surfactants and some commercial soap/detergent products using suspended TiO<sub>2</sub> catalysts. *J. Mol. Catal. A:Chem.*, 104, L197-L199.
- Read, H.W., Fu, X., Clark, L.A., Anderson, M.A., & Jarosch, T. (1996). Field Trials of a TiO<sub>2</sub> Pellet-based Photocatalytic Reactor for Off-gas Treatment of a Soil Vapor Extraction Well. *J. Soil Contam.*, 5, 187-202.
- Richard, C., & Bengana, S., (1996). pH effect in the photocatalytic transformation of a phenyl-urea herbicide. *Chemosphere*, 33, 635-641.



- Sabin, F., Turk, T., & Vogler, A., (1992). Photo-oxidation of organic compound in the presence of titanium dioxide: determination of the efficiency. *J. Photochem. Photobiol. A:Chem.*, 63, 99-106.
- Sakai, N., Wang, R., Fujishima, A., Watanabe, T., & Hashimoto, K., (1998). Effect of Ultrasonic Treatment on Highly Hydrophilic TiO<sub>2</sub> Surfaces. *Langmuir*, 14, 5918-5920.
- Sakkas, V.A., Arabatzis, I., Konstantinou, I.K., Dimou, T.A., Albanis, T.A., & Falaras, P., (2004). Metolachlor photocatalytic degradation using TiO<sub>2</sub> photocatalysts. *Appl. Catal B: Environ.*, 49, 195-205.
- Sakkas, V.A., Lambropoulou, D.A., Sakellarides, T.M., & Albanis, T.A., (2002). Application of solid phase microextraction (SPME) during the photocatalytic treatment of fenthion and ethyl parathion in aqueous TiO<sub>2</sub> suspensions. *Anal. Chim. Acta*, 467, 233-243.
- Sakthivel, S., Neppolian, B., Shankar, M.V., Arabindoo, B., Palanichamy, M., & Murugesan, V., (2003). Solar photocatalytic degradation of azo dye: Comparison of photocatalytic efficiency of ZnO and TiO<sub>2</sub>. *Sol. Energy Mater. Sol. Cells.*, 77, 65-82.
- Sanlaville, Y., Guittonneau, S., Mansour, M., Feicht, E.A., Meallier, P., & Kettrup, A., (1996). Photosensitized degradation of terbuthylazine in water. *Chemosphere*, 33, 353-362.
- Saqui, M., & Muneer, M., (2002). Semiconductor mediated photocatalysed degradation of an anthraquinone dye, remazol brilliant blue R under sunlight and artificial light source. *Dyes and Pigm.*, 53, 237-249.
- Saqui, M., & Muneer, M., (2003). Photocatalytic degradation of two selected textile dye derivatives, eosin yellowish and p-rosaniline in aqueous suspensions of titanium dioxide. *J Environ Sci Health A.*, 38, 2581-2598.
- Schmelling, D.C., Gray, K.A., & Kamat, P.V., (1996). The role of reduction in the photocatalytic degradation of TNT. *Environ. Sci. Technol.*, 30, 2547-2555.
- Shifu, C., & Yunzhang, L., (2007). Study on the photocatalytic degradation of glyphosate by TiO<sub>2</sub> photocatalyst. *Chemosphere.*, 67, 1010-1017.
- Singh, H.K., Saqui, M., Haque, M.M., & Muneer, M., (2007b). Heterogeneous photocatalysed degradation of 4-chlorophenoxyacetic acid in aqueous suspension. *J. Hazard. Mater.*, 142, 374-380.
- Singh, H.K., Saqui, M., Haque, M.M., Muneer, M., & Bahnemann, D.W., (2007a). Titanium dioxide mediated photocatalysed degradation of phenoxyacetic acid and 2,4,5-trichlorophenoxyacetic acid in aqueous suspensions. *J. Mol. Catal. A: Chem.*, 264, 66-72.
- Sleiman, M., Ferronato, C., Fenet, B., Baudot, R., Jaber, F., and Jean-Marc C., (2006). Development of HPLC/ESI-MS and HPLC/<sup>1</sup>H NMR Methods for the Identification of Photocatalytic Degradation Products of Iodosulfuron. *Anal. Chem.*, 78, 2957-2966.
- Stapleton, D.R., Konstantinou, I.K., Mantzavinos, D., Hela, D., & Papadaki, M., (2010). On the kinetics and mechanisms of photolytic/TiO<sub>2</sub>-photocatalytic degradation of substituted pyridines in aqueous solutions. *Appl. Catal. B: Environ.*, 95, 100-109.
- Sturini, M., Fasani, E., Prandi, C., Casaschi, A., & Albini, A., (1996). Titanium-dioxide photocatalysed decomposition of some thiocarbamates in water. *J. Photochem. Photobiol. A: Chem.* 101, 251-255.

- Tamimi, M., Qourzal, S., Assabbane, A., Chovelon, J.-M., Ferronato, C., & Ait-Ichou, Y., (2006). Photocatalytic degradation of pesticide methomyl: determination of the reaction pathway and identification of intermediate products. *Photochem. Photobiol. Sci.*, 5, 477-482.
- Tanaka, K., Robledo, S.M., Hisanaga, T., Ali, R., Ramli, Z., & Bakar, W.A., (1999), Photocatalytic degradation of 3,4-xylyl N-methylcarbamate MPMC/ and other carbamate pesticides in aqueous TiO<sub>2</sub> Suspensions. *J. Mol. Catal. A: Chem.*, 144, 425-430.
- Topalov, A., Molnár-Gábor, D., Kosani, M., & Abramovi, B., (2000). Photomineralization of the herbicide mecoprop dissolved in water sensitized by TiO<sub>2</sub>. *Water. Res.*, 34, 1473-1478.
- Tseng, J.M., & Huang, C.P., (1991). Removal of Chlorophenols from Water by Photocatalytic Oxidation. *Water Sci. Technol.* 23, 377-387.
- Vaz, J.L., Boussaoud, B., Ichou, Y.A., & Petit-Ramel, M., (1998). Photomineralization on titanium dioxide of uracil and 5-halogenouracils. Influence of pH and some anions on the photodegradation of uracil. *Analysis*, 26, 83-87.
- Vidal, (1998). Developments in solar photocatalysis for water purification. *Chemosphere*, 36, 2593-2606.
- Vidal, A. Dinya, Z., Mogyorodi Jr, F., & Mogyorodi, F., (1999). Photocatalytic of thiocarbamate herbicide active ingredients in water. *Appl. Catal. B: Environ.*, 21, 259-267.
- Vidal, A., & Martin Luengo, M.A., (2001). Inactivation of titanium dioxide by sulphur: Photocatalytic degradation of vapam. *Appl. Catal. B: Environ.*, 32, 1-9.
- Vinodgopal, K., Wynkoop, D.E., & Kamat, P.V., (1996). Environmental Photochemistry on semiconductor surfaces: A photosensitization approach for the degradation of a textile azo dye, Acid Orange 7. *Environ. Sci. Technol.*, 30, 1660-1666.
- Vulliet, E., Emmelin, C., Chovelon, J.M., Guillard, C., & Herrmann, J.M., (2002). Photocatalytic degradation of sulfonylurea herbicides in aqueous TiO<sub>2</sub>. *Appl. Catal. B: Environ.* 38, 127-137.
- Wang, R., Hashimoto, K., Fujishima, A., Chikuni, M., Kojima, E., Kitamura, A., Shimohigoshi, M., & Watanabe, T., (1998). Photogeneration of Highly Amphiphilic TiO<sub>2</sub> Surfaces. *Adv. Mat.*, 10, 135-138.
- Wang, R., Sakai, N., Fujishima, A., Watanabe, T., & Hashimoto, K., (1999). Studies of Surface Wettability Conversion on TiO<sub>2</sub> Single-Crystal Surfaces. *J. Phys. Chem. B.*, 103, 2188-2194.
- Wardman, P. (1989). Reduction potentials of one-electron couples involving free radicals in aqueous solution. *J. Phys. Chem.*, Ref. Data, 18, 1637-1755.
- Weichgrebe, D., & Vogelpohl, A. (1995) Strategie zur Auswahl geeigneter Oxidationsverfahren. 2. Fachtagung Naboxidative Abwasserbehandlung, Clausthal.
- Weller, H., (1993). Kolloidale Halbleiter-Q-Teilchen: Chemie im Übergangsbereich zwischen Festkörper und Molekül. *Angew. Chem. Int. Ed. Eng.*, 32, 41-53.
- Yu, J.C., Yu, J., Ho, W., & Zhao, J., (2002). Light-induced super-hydrophilicity and photocatalytic activity of mesoporous TiO<sub>2</sub> thin films. *J. Photochem. Photobiol. A:Chem.*, 148, 331-339.

- Zalenska, A., Hupta, J., Wiergowski, M., & Biziuk, M., (2000). Photocatalytic degradation of lindane, p,p'-DDT and methoxychlor in an aqueous environment . *J.Photochem. Photobiol. A: Chem.* 135, 213-220.
- Zhang, P., Scrudato, R.J., & Germano, G., (1994). Solarcatalytic inactivation of *Escherichia coli* in aqueous solutions using TiO<sub>2</sub> as catalyst. *Chemosphere*, 28, 607-611.
- Zhu, X., Feng, X., Yuan, C., Cao, X., & Li, J., (2004). Photocatalytic degradation of pesticide pyridaben in suspension of TiO<sub>2</sub>: identification of intermediates and degradation pathways. *J. Mol. Catal. A: Chem.*, 214, 293-300.



## **Organic Pollutants Ten Years After the Stockholm Convention - Environmental and Analytical Update**

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Ten years after coming into force of the Stockholm Convention on Persistent Organic Pollutants (POPs), a wide range of organic chemicals (industrial formulations, plant protection products, pharmaceuticals and personal care products, etc.) still poses the highest priority environmental hazard. The broadening of knowledge of organic pollutants (OPs) environmental fate and effects, as well as the decontamination techniques, is accompanied by an increase in significance of certain pollution sources (e.g. sewage sludge and dredged sediments application, textile industry), associated with a potential generation of new dangers for humans and natural ecosystems. The present book addresses these aspects, especially in the light of Organic Pollutants risk assessment as well as the practical application of novel analytical methods and techniques for removing OPs from the environment. Providing analytical and environmental update, this contribution can be particularly valuable for engineers and environmental scientists.

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