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Influence of Parameters on the Heterogeneous Photocatalytic Degradation of Pesticides and Phenolic Contaminants in Wastewater: A Short Review

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ABSTRACT

In recent years, the application of heterogeneous photocatalytic water purification process has gained wide attention due to its effectiveness in degrading and mineralizing the recalcitrant organic compounds as well as the possibility of utilizing the solar UV and visible light spectrum. This paper aims to review and summarize the recently published works on the titanium dioxide (TiO_2) photocatalytic oxidation of pesticides and phenolic compounds, predominant in storm and waste water effluents. The effect of various operating parameters on the photocatalytic degradation of pesticides and phenols are discussed. Results reported here suggested that the photocatalytic degradation of organic compounds depends on the type of photocatalyst and composition, light intensity, initial substrate concentration, amount of catalyst, pH of the reaction medium, ionic components in water, solvent types, oxidizing agents/electron acceptors, catalyst application mode, and calcinations temperature in water environment. A substantial amount of research has focused on the enhancement of TiO_2 photocatalysis by modification with metal, non-metal and ion doping. Recent developments in TiO_2 photocatalysis for the degradation of various pesticides and phenols are also highlighted in this review. It is evident from the literature survey that photocatalysis has shown good potential for the removal of various organic pollutants. However, still there is a need to find out the practical utility of this technique on commercial scale.

Key Words: Pesticide; Herbicide; Phenol; Photocatalysis, and Water Purification

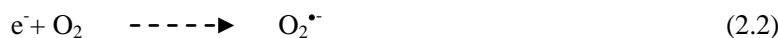
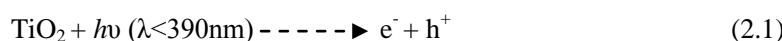
1. Introduction

Reuse and recycling of storm and wastewater effluent is a key approach in a sustainable water management portfolio by water utilities both in Australia and in other parts of the world to minimize the growing water demand in a water scarce environment (Mitchell et al.2002, DEH 2002, Radcliff 2006). The frequent occurrence of pesticides and phenolic compounds in wastewater and associated environmental hazards has heightened concerns over public health due to their high toxicity and bio-recalcitrant structure (Eriksson et al.2007). These contaminants are being continuously released into the aquatic environment through various anthropogenic inputs. The detection of toxic organic compounds in storm and waste water effluent is reported to be a major obstacle as regards wide ranging acceptance of water recycling (DEC2006, Mahmoodi et al.2007). Further, their variety, toxicity and persistence can directly impact the health of ecosystem and present a threat to humans through contamination of drinking water supplies e.g surface and ground water (DEH2002, Eriksson et al.2007). The response has been the drive to achieve efficient removal of persistent organic pollutants from waste water effluent to lessen the risk of pollution

problems from such toxic chemicals to enable its reuse. Consequently, considerable efforts have been devoted to developing a suitable purification method that can easily destroy these bio-recalcitrant organic contaminants. Due to their incomplete removal during wastewater treatment, they are ubiquitous in secondary wastewater effluents, river and lakes at low concentration. Despite their low concentration, these contaminants are of a major health concern due to their extremely high endocrine disrupting potency and geno toxicity ([Arques et al.2007](#)). These findings enunciate the necessity for further research on the removal of trace contaminants to minimize their accumulation, particularly prior to indirect or direct reuse of reclaimed water. Moreover, the conventional wastewater purification systems also generate wastes during the treatment operation, which requires additional steps and cost. Heterogeneous photocatalytic oxidation (HPO) process employing catalyst such as TiO₂, ZnO etc., and UV light has demonstrated promising results for the degradation of persistent organic pollutants, and producing more biologically degradable and less toxic substances ([Garica et al.2006,2008;Vora et al.2009](#)). This process is mainly dependent on the in-situ generation of hydroxyl radicals under ambient conditions which are capable of converting a wide spectrum of toxic organic compounds including the non-biodegradable one into relatively innocuous end products such as CO₂, H₂O. In HPO process, the combined action of semiconductor photocatalyst, an energetic radiation source and an oxidizing agent governs the destruction of recalcitrant organics. Moreover, the process can be driven by solar UV and visible light. Near the earth surface, the sun produces 0.2-0.3 mol photons m⁻²h⁻¹ in the range of 300-400nm with a typical UV flux of 20-30 Wm⁻². This suggests for using the sunlight as an economically and ecologically sensible light source ([Goslich et al.1997](#)). As a result, development of efficient photocatalytic water purification process for large scale applications has received substantial interest but still it remains a challenge. Although heterogeneous photocatalysis appeared in numerous forms, photocatalytic degradation of pesticides and phenolic compounds has recently been most widely investigated. However, low quantum efficiency due to inefficient visible light harvesting catalyst ([Adesina 2004](#)), the design of photoreactor ([Mukherjee and Ray 1999](#)), the recovery and reuse of titanium dioxide ([Adesina 2004](#)) the generation of toxic intermediates ([Konstantinou and Albanis 2003; Moctezuma et al.2007](#)), as well as concern about catalyst deactivation ([Legrini et al.1993](#)) are reported to be the major drawbacks. Results presented here indicate that the photocatalytic degradation of pesticides and phenolic compounds is largely dependent on the solution pH, types of catalyst and composition, organic substrate type and concentration, light intensity, catalyst loading, ionic composition of waste water, types of solvent, oxidant concentration, and calcinations temperature ([Shaktivel et al.2003](#)). Understanding the impacts of various parameters on the photocatalytic degradation efficiency is of paramount importance from the design and the operational points of view when choosing a sustainable and efficient technique for the treatment of waste water. This paper aims to present an overview of recent studies on TiO₂ photocatalytic oxidation process with particular emphasis on the role of important operating parameters on the photocatalytic degradation of pesticides and phenolic compounds together with recent achievements. Recent advances in TiO₂ and ZnO photocatalysis for pesticides and phenols degradation using metal, non-metal and ion doping is also highlighted in this review. The existing limitations and future research needs to utilize TiO₂ photocatalysis for water treatment is also discussed.

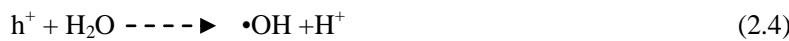
2. Principle of Photocatalytic Oxidation Process

In the photocatalytic oxidation process, organic pollutants are destroyed in the presence of semiconductor photocatalysts (e.g., TiO₂, ZnO) an energetic light source, and an oxidising agent such as oxygen or air. As illustrated in Fig.1, only photons with energies greater than the band-gap energy (ΔE) can result in the excitation of valence band (VB) electrons which then promote the possible reactions with organic pollutants. The absorption of photons with energy lower than ΔE or longer wavelengths usually causes energy dissipation in the forms of heat. The illumination of the photocatalytic surface with sufficient energy, leads to the formation of a positive hole (h^+) in the valence band and an electron (e^-) in the conduction band (CB). The positive hole oxidizes either pollutant directly or water to produce hydroxyl radical $\cdot OH$, whereas the electron in the conduction band reduces the oxygen adsorbed on the photocatalyst (TiO₂). The activation of TiO₂ by UV light can be represented by the following steps.

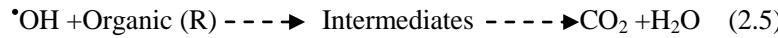


In this reaction, h^+ and e^- are powerful oxidizing and reductive agents, respectively. The oxidative and reductive reaction steps are expressed as,

Oxidative reaction:



Reductive reaction:



Hydroxyl radical generation by the photocatalytic oxidation process is shown in the above steps. In the degradation of organic pollutants, the hydroxyl radical generated from the oxidation of adsorbed water where it is adsorbed as OH⁻, is the primary oxidant; and the presence of oxygen can prevent the recombination of an electron-hole pair. The $\cdot OH$ attacks organic compounds e.g. chlorinated aromatics, aniline and nitrophenols which result in various reaction intermediates depending on the nature of the compounds. The resulting intermediates further react with $\cdot OH$ to produce final degradation products such as CO₂ and H₂O. In the photocatalytic degradation of pollutants, when the reduction process of oxygen and the oxidation of pollutants do not advance simultaneously, there is an electron accumulation in the CB, thereby causing an increase in the rate of recombination of e^- and h^+ (Hoffman et al.1995, Hermann 1999). Thus it is of paramount importance to prevent electron accumulation in efficient photocatalytic oxidation. In photocatalysis, TiO₂ is by far the most widely studied system due to its high activity, desirable physical and chemical properties, low cost, and availability. Of three common TiO₂ crystalline forms, anatase and rutile forms have been investigated extensively as photocatalysts. Anatase has been reported to be more active as a photocatalyst than rutile. Similar oxidation pathways to those of TiO₂ are confirmed in ZnO photocatalyst including the formation of $\cdot OH$ radical and the direct oxidation by photogenerated holes, etc. ZnO is reported to be as reactive as TiO₂ under concentrated sunlight, since the band gap energy of ZnO is equal to that of TiO₂, i.e., 3.2eV. Some other metal oxides including CeO₂,

SnO_2 , WO_3 and CdS have also been examined for organic contaminants degradation ([Swarnalatha and Anjaneyulu 2004; Ji et al.2008, 2009; Lin et al.2008](#)). At low substrate concentration, the photocatalytic degradation rate of organic compounds can be explained by a pseudo-first order pattern, with the following equation demonstrating the relationship of C and t

$$\ln \frac{C}{C_0} = k_{\text{obs}} t,$$

where k_{obs} is the apparent reaction rate constant, t the reaction time, C_0 the initial concentration of target pollutant in aqueous solution and C is the residual concentration of pollutant at time t . Different light sources such as UV lamps and solar radiation have been used in the photocatalytic degradation of various pesticides and herbicides dominant in storm water and wastewater effluent ([Bahnemann et al.2007, Lachheb et al.2008](#)).

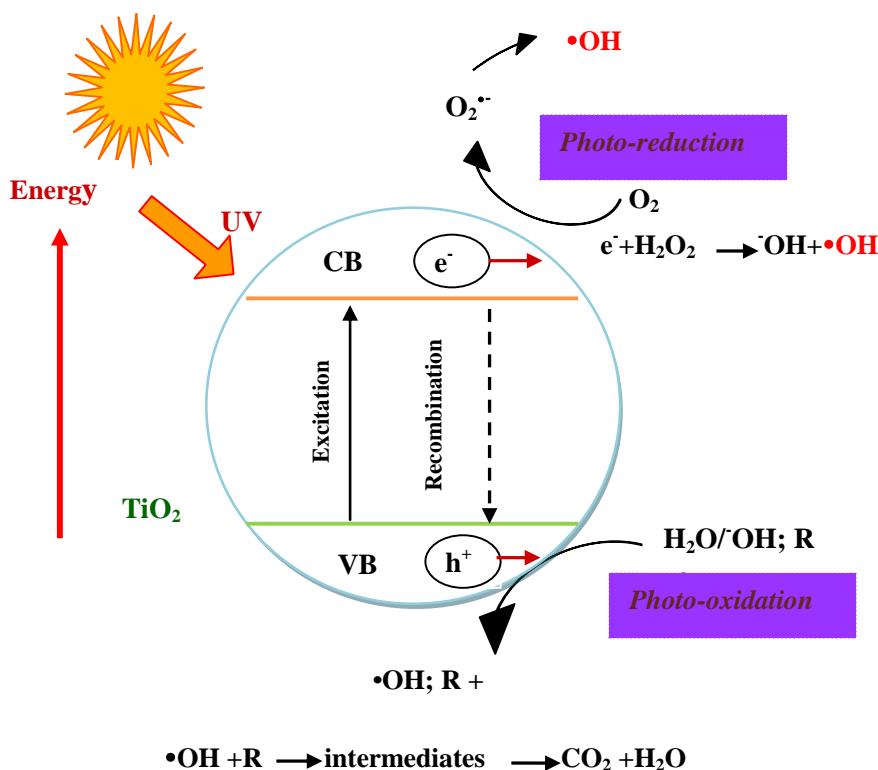


Fig.1 Schematic diagram illustrating the principle of TiO_2 photocatalysis

3. Effect of operating parameters on the degradation of pesticides and phenols

3.1 Types and Composition of Photocatalyst

The photocatalytic activity of TiO_2 depends on surface and structural properties of semiconductor such as crystal composition, surface area, particle size distribution, porosity, band gap and surface hydroxyl density. Particle size is of primary importance in heterogeneous catalysis, because it is directly related to the efficiency of a catalyst through the definition of its specific surface area. A number of commercially

available catalysts have been tested for the photocatalytic degradation of various organic compounds in aqueous environment. Table 1 presents the specification and characteristics of some commercial TiO₂ samples. The photocatalyst titanium dioxide Degussa P-25 has been widely used in most of the experimental conditions; other catalyst powders, namely, Hombikat UV100, PC 500, PC10, PC 50, Rhodia and Travancore Titanium Products (TTP), India, were also used for degradation of toxic organic compounds (Bahnemann et al.2007; Singh et al.2004,2007b; Erquez and Pichat 2006). P-25 contains 75% anatase and 25% rutile with a specific BET surface area of 50m²/g and a primary particle size of 20 nm. Hombikat UV 100 consists of 100% pure and smaller anatase with a specific BET surface area of 250m²/g and a primary particle size of 5 nm. The photocatalyst PC 500 has a BET surface area of 287m²/g with 100% anatase and primary particle size of 5-10nm and TiO₂ obtained from TTP, India has a BET surface area of 9.82m²/g. It has been demonstrated that the degradation rate of dyes proceeds much more rapidly in the presence of P-25 as compared to other photocatalysts. The efficiency of photocatalysts was shown to follow the order: P-25> UV100> PC500> TTP for the degradation of various pesticides and herbicides derivatives (Singh et al.2003,2004, 2007a,2007b, Rahman and Muneer 2005a, 2005b; Qamar and Muneer 2005). The differences in the photocatalytic activity are likely to be related to the differences in the BET surface, impurities, lattice mismatches or density of hydroxyl groups on the catalyst's surface, since these factors could affect the adsorption behavior of a pollutant or intermediate molecule and the life time and recombination rate of electron-hole pairs (Bahnemann et al. 2007, Singh et al. 2007a, 2007b, 2007c, Rahman and Muneer 2005a, 2005b; Qamar and Muneer 2005, Muneer and Bahnemann 2002). Swarnalatha and Anjaneyulu 2004 compared the photocatalytic efficiency of P25, TiO₂ (Merck), ZnO, CdS and WO₃ for photocatalytic degradation of 1×10^{-4} M 2,6-dinitrophenol(2,4-DNP). In the presence of UV light (254nm) and 4g/L catalyst dose, the degradation rate was shown to follow the order: P25> ZnO> TiO₂ (Merck)> CdS> WO₃. The observed low activity of CdS and WO₃ is related to its smaller band gap.

Table 1 Specification and characteristics of TiO₂ samples

Sample	Specific surface area BET (m ² /g)	Crystal size (nm)	Composition	Ref.
P-25	50	21	75% Anatase, 25% Rutile	Singh et al 2007b
PC 500	287	5-10	100% Anatase	Singh et al 2007b
UV 100	250	5	100% Anatase	Singh et al 2007b
TTP	9.82	N/A	N/A	Singh et al 2007b
PC 10	10	65-75	100% Anatase	Erquez and Pichat 2006
PC 50	54	20-30	100% Anatase	Erquez and Pichat 2006
Rhodia	150	N/A	100% Anatase	Erquez and Pichat 2006

N/A= Not available

In comparison to UV 100, P-25 was reported to be efficient for the degradation of prometryn (Evgenidou et al.2007). The photocatalytic activity of Degussa P-25 was reported to be higher due to slow recombination between electron and holes whereas Hombikat UV 100 has a high photoreactivity due to

fast interfacial electron transfer rate. The higher photoactivity of P-25 has been attributed to its crystalline composition of rutile and anatase. It was postulated that the smaller band gap of rutile absorbs the photons and generates electron-hole pairs. Then the electron transfer takes place from the rutile CB to electron traps in anatase phase (Hurun et al.2003). Thus it inhibits the recombination and allows the hole to move to the surface of the particle to react (Hurun et al.2003). Poulios and Kositzi 2006 studied the photocatalytic oxidation of methomyl by comparing the efficiency of P-25, ZnO and UV-100. Under the conditions investigated, the order of the photocatalytic dissolved organic carbon (DOC) reduction of methomyl was reported to be: P-25>ZnO>UV100. The photocatalytic degradation of vanillin is demonstrated in the order: P-25> UV100> ZnO (Qamar and Muneer2009). Under the tested conditions, the photocatalytic degradation of 4-Chlorophenol (4-CP) was shown to follow the order: P25> PC10> PC50> PC500> Rhodia (Erquez and Pichat 2006). Salah et al.2004 compared the efficiency of three commercial catalysts P-25(20nm), A1(160nm) and A2(330nm) available in anatase form, and ZnO for the degradation of phenol. After 5h reaction, the order of the efficiency was shown to follow ZnO>P-25>A1>A2. Valenzuela et al.2002 compared the photocatalytic activity of ZnO, Fe₂O₃ and ZnFe₂O₄ for the degradation of phenol. After 100 min irradiation, the observed degradation from the samples calcined at 800°C was shown to follow the order TiO₂ P-25> ZnFe₂O₄> ZnO> Fe₂O₃.

3.2 Influence of substituent group

Lapertot et al.2006 investigated the influence of the halogen substituent on the photocatalytic degradation of the *p*-halophenols by comparing their apparent rate constants. The observed order was found to decrease in the order as follows: *p*-fluorophenol≈*p*-chlorophenol≈phenol >*p*-bromophenol >*p*-iodophenol. This was related to the electron density on the aromatic ring, which varies with the halogen substituent. In suspended form, Lacheb et al.2008 reported that in comparison to PC 500, P-25 was more efficient for the degradation of phenols and poly nitrophenols(4-NP, 2,4-DNP,2,4,6-TNP) in the presence of either artificial or solar light. The photocatalytic degradation of the tested compounds were shown in the following order: 2,4,6-TNP> 2,4-DNP> 4-NP> Phenol. However, they observed a different order: phenol <4-NP <2, 4-DNP <2, 4, 6-TNP for PC 500 supported on Ahstrom paper 1048. The difference was related to the variation in adsorption behaviour. The photocatalytic degradation of phenol and ortho-substituted phenolic compounds was shown to follow the order: Guaiacol> 2-chlorophenol= Phenol>Catechol (Peiro et al.2001). Kusvuran et al.2005 studied the photocatalytic degradation of 2,4,6-trimethylphenol (TMP), 2,4,6-trichlorophenol (TCP), 2,4,6-tribromophenol (TBP), 2,4-dimethylphenol (DMP), 2,4-dichlorophenol (DCP)and 2,4-dibromophenol (DBP). Under the conditions tested, degradation of these tri-substituted phenols is found to be in the following order: TCP> TBP> TMP. and the degradation of di-substituted phenols is shown to be in the order: DCP> DBP> DMP. Under the experimental conditions, Baran et al.2008 indicated that the pattern of photocatalytic degradation of Acid Black1 (AB1), Acid Orange 7(AO7), and Basic Orange 66 (BO66) dyes (Co=0.1mM) follows the order: BO66 > AO7> AB1. This was attributed to the variation in adsorption behaviour due to different chemical structures.

3.3 Light Intensity and wave length

Light intensity determines the extent of light absorption by the semiconductor catalyst at a given wavelength. The rate of initiation of photocatalysis, electron-hole formation in the photochemical reaction is strongly dependent on the light intensity (Cassano and Alfano 2000). Light intensity distribution within the reactor invariably determines the overall pollutant conversion and degradation efficiency (Pareek et al.2008). Consequently the dependency of pollutant degradation rate on the light intensity has been studied in numerous investigations of various organic pollutants. While in some cases the reaction rate exhibited a square root dependency on the light intensity, others observed a linear relationship between the two variables (Terzian and Serpone 1991). Ollis 1991 reviewed the effect of light intensity on the organic pollutant degradation rate. It has been reported (Ollis 1991, Al-Sayed et al.1991, Hermann 1999) that the rate was proportional to the radiant flux Φ for $\Phi < 25\text{mW/cm}^2$, above 25mW/cm^2 , the rate was shown to be varied as $\Phi^{1/2}$, indicating a too high value of the flux and an increase of the electron-hole recombination rate. At high intensity, the reaction rate is independent of light intensity. This is likely because at low intensity reactions involving electron-hole formation are predominant and electron-hole recombination is insignificant. Wong et al.2003 studied the photocatalytic degradation of alachar using three different UV lamps at 254, 300 and 350nm. Of the three UV wavelengths used, the highest photocatalysis quantum yield was obtained at 300nm. The degradation rate constant of chlorsulfuron was reported to increase from 0.074 min^{-1} to 0.28 min^{-1} when the radiant flux increases from 6.9 mW/cm^2 to 33.8 mW/cm^2 (Freshno et al.2005). In the case of pyridaben degradation, a linear relation between reaction rate k and radiant flux was reported to exist for the range of radiant flux studied from 2.8 to 8.8 mW/cm^2 (Zhu et al.2005). Under the tested conditions, they also noticed that photocatalytic degradation of pyridaben was more efficient at $\lambda \geq 300\text{nm}$ than at $\lambda \geq 360\text{nm}$ irradiation. The degradation rate of atrazine in an immobilized reactor was independent of UVA ($\lambda_{\text{max}}=365\text{nm}$, $I=3.28\times 10^{-8}\text{ Einstein cm}^{-2}\text{s}^{-1}$) and UVB ($\lambda_{\text{max}}=313\text{nm}$, $I=2.0\times 10^{-8}\text{ Einstein cm}^{-2}\text{s}^{-1}$) irradiation, however, the maximum apparent quantum yield under UVB was higher compared to UVA irradiation (McMurray et al.2006).

Para et al.2004 indicated the dependence of atrazine degradation rate on the intensity of incident light from the Suntest solar simulator. Photocatalytic degradation rate constants of Imazapyr were indicated to be directly proportional to the radiation intensity from 0 to 25 mW/cm^2 (Carrier et al.2006). A faster degradation was obtained with intensity at 90mW/cm^2 as compared to a light intensity of 50mW/cm^2 . Similar trends have been indicated for the degradation of carbofuran (Mahalakshmi et al.2007), cyromazine (Gutailler et al.2001) with increase in irradiation light intensity from 16 to 64W. Chen et al 2007 also examined that the effect of UV lamp power on the photocatalytic degradation of dimethoate. The degradation efficiency has been shown to be higher under irradiation of a 500W (80.15%) lamp compared to a 300W (37.07%) lamp. With increase in lamp power (and thus its light intensity) the rate of electron-hole pair formation at the TiO_2 surface increases and consequently its ability to oxidize organic pollutant. Vulliet et al. 2003 studied the effect of photon flux on the photocatalytic degradation of sulfonylurea

herbicides. The reaction rate was shown to be proportional to the incident photon flux when photons flux $\leq 4.2 \times 10^{-16}$ photons s⁻¹. The degradation rate was reported to vary as the square root of the radiant flux until 12.6×10^{-16} photons s⁻¹. Sleiman et al. 2007 observed that the first order rate constant of iodosulfuron degradation is directly proportional to the photon flux when flux is below 10^{16} photon s⁻¹cm⁻². At high photon flux, the rate constant was shown to vary as the square root of flux. It has been indicated that the build-up of electron-hole pairs within the photocatalyst is smaller than the oxidizable organic substrate concentration and hence a linear rate law was observed at low fluxes whereas the phototocatlytic degradation efficiency was shown to be limited to the electron-hole recombination which is predominant at flux above 10^{16} photon s⁻¹cm⁻². Kaneco et al. 2009 investigated the effect of irradiance on the solar photocatalytic destruction of thiram with various light intensities on sunny and cloudy days. The degradation efficiency increased rapidly with increase in the light intensity up to 0.4mW/cm², and above the intensity the efficiency increased gradually. Puma et al. 2002 examined the effect of light wavelength on the photocatalytic degradation of 2-chlorophenol (2-CP) using UV-A alone and simultaneous UV-A, B, and C radiation. The rate of degradation and mineralization of 2-CP were significantly improved with UV-ABC radiation compared to UV-A radiation. The rate improvement was related to the combined use of photolysis, photocatalysis, and synergistic effects due to associated photolysis and photocatalysis. The solar photocatalytic degradation efficiency of bisphenol A (BPA) is reported to increase rapidly with increase in the light intensity up to 0.35mW/cm², and then the efficiency increased gradually (Kaneco et al. 2004). Venkatachalam et al. 2007a compared the mineralization efficiency of 4-CP using the lamps of wavelength 365nm and 254nm over TiO₂. The mineralization rate at 365nm is reported to be slightly higher than at 254 nm. The observed lower degradation rate at 254 nm was attributed to the partial absorption and wasting of light at 254nm by 4-CP itself. Pourata et al. 2009 tested the effect of light intensity (5.3-17.5Wm⁻²) on the photooxidative removal of bentazon and achieved the highest removal at 17.5Wm⁻². Chiou et al. 2008 reported the effect of UV light intensity (20-400W) on the photocatalytic degradation of phenol. The degradation rate constants with a light intensity of 20, 100, and 400W are shown to be 8.3×10^{-3} , 0.012 and 0.031min⁻¹, respectively. Under the conditions tested, an acceptably good linear correlation exists between the apparent first order rate constant and light intensity. The studies reviewed here suggested that the effect of light intensity on the photocatalytic degradation rate must be determined to ensure successful application of photocatalytic oxidation system.

3.4 Pollutant type and concentration

Successful application of photocatalytic oxidation system requires the investigation of the dependence of photocatalytic degradation rate on the substrate concentration (Co). Table 2 summarizes a variety of pesticides and phenolic compounds studied under various initial concentrations. The photocatalytic degradation rate of phosphamidon was shown to increase with the increase in initial concentration from 1×10^{-4} to 4.5×10^{-4} M (Rabindranathan et al. 2003). However, at concentration of 6×10^{-4} M, the rate slows down considerably. Similar trends have been observed for the photocatalytic degradation of triclopyr and

daminozid (Qamar et al.2006), carbofuran(Mahalakshmi et al.2007), prophan and tebuthioron (Muneer et al.2005), Indole -3-acetic acid and Indole-3-buteric acid (Qamar and Muneer 2005), methamidophos (Wei et al.2009), methyl parathion (Kim et al.2006), 4-chlorophenol (Venkatachalam et al.2007). Using ZnO, Pardeshi and Patil 2009 tested the effect of initial concentration (50-300ppm) on the photocatalytic degradation of resorcinol under solar light. The degradation efficiency in 7h decreases from 100 to 43.8% as the Co increases from 100 to 300 ppm. Consistently similar results have been reported for degradation of phenol (Pardeshi and Patil 2008), thiram (Kaneco et al.2009), lindane (Senthilnathan and philip2010), dimethoate (Chen et al.2007), diazinon and erioglaucino (Daneshvar et al.2006,2007), Bentazon(Pourata et al.2009), 2-chlorophenol (Barakat et al.2005).

Table 2 Influence of initial pollutant concentration on the photocatalytic degradation of various pollutants

Pollutant	Light source	Photocatalyst	Co range, mM	Optimum Co, mM	Ref.
Phosphamidon	UV	TiO ₂	0.1-0.6	0.45	Rahman and Muneer 2005
Acephate	UV	TiO ₂	0.7-1.0	1	Rahman et al.2006
Diphenamid	UV	TiO ₂	0.1-0.6	0.6	Rahman et al.2003
Phenol	Solar	ZnO	0.027-0.32	0.027	Pardeshi and Patil 2008
2,4-dinitrophenol	UV	ZnO	0.05-0.09	0.09	Vora et al.2009
Carbofuran	UV	TiO ₂	0.023-0.113	0.09	Mahalakshmi et al.2007
Thiram	Solar	TiO ₂	4.2×10^{-4} - 16.6×10^{-4}	4.2×10^{-4}	Kaneco et al.2009
Indole-3-acetic acid	UV	TiO ₂	0.2-0.6	0.3	Qamar and Muneer 2005
Indole-3-buteric acid	UV	TiO ₂	0.18-0.6	0.3	Qamar and Muneer 2005
Lindane	Visible	N-TiO ₂	3.45×10^{-5} - 2.07×10^{-4}	3.45×10^{-5}	Senthilnathan and Philip 2010
Dimethoate	UV	TiO ₂	0.0195-0.49	0.0195	Chen et al.2007
Isoproturon	Solar	TiO ₂	0.25-.75	0.75	Haque and Muneer 2003
Triclopyr	UV	TiO ₂	0.25-1.0	0.75	Qamar et al. 2006
Daminozid	UV	TiO ₂	0.50-1.5	0.75	Qamar et al. 2006
Diazinon	UV	ZnO	0.003-0.005	0.003	Daneshvar et al.2007
Methamidophos	UV	Re-TiO ₂	0.1-0.5	0.1	Zhang et al.2009
2-chlorophenol	UV	Co-TiO ₂	0.097-0.583	0.097	Barakat et al.2005
Resorcinol	Solar	ZnO	0.05-0.272	0.05	Pardehsi and Patil 2009
Erioglaucine	UV	TiO ₂	0.006-0.02	0.006	Daneshvar et al.2006
Bentazon	UV	TiO ₂	0.02-0.062	0.02	Pourata et al.2009
Prophan	UV	TiO ₂	0.25-1.3	0.75	Muneer et al.2005
Propachlor	UV	TiO ₂	0.2-1.35	1.35	Muneer et al.2005
Tebuthioron	UV	TiO ₂	0.25-1.5	1.0	Muneer et al.2005

Parida and Parija 2006 examined the effect of initial substrate concentration (2-25g/l) on the photocatalytic degradation of phenol under sunlight, visible and UV light, respectively. With the increase in the substrate concentration, the degradation efficiency decreased from 100 % to 60% under solar irradiation. Under UV light, the degradation was reported to decrease from 94 % to 52% with increasing initial concentration. The degradation was found to decrease from 95 % to 50% under visible light. The photocatalytic degradation of 4-nitrophenol (4-NP) was shown to decrease from 100 to 40.9% as the initial concentration increases from 0.02 to 0.1g/L (Parida et al.2006). Lathasree et al.2004 studied the effect of initial concentration (40-100ppm) on the photocatalytic degradation of phenol using ZnO as catalyst. The initial rates of photodegradation were high at lower concentration range but it decreased as concentration increased. The degradation was found to follow first order kinetics. For chlorophenols, the initial rate was observed to increase with the increase in the initial concentration range of 40-60 ppm and decreased as concentration increased further. As indicated in several investigations that as the concentration of the target pollutant increases, more and more molecules of the compound are adsorbed on the surface of the photocatalyst. Therefore, the reactive species ($\bullet\text{OH}$ and $\bullet\text{O}_2^-$) required for the degradation of the pollutant also increases. However, the formation of $\bullet\text{OH}$ and $\bullet\text{O}_2^-$ on the catalyst surface remains constant for a given light intensity, catalyst amount and duration of irradiation. Hence, the available OH radicals are inadequate for pollutant degradation at higher concentrations. Consequently the pollutant degradation rate decreases as the concentration increases (Bahnemann et al.2007). In addition, an increase in substrate concentration can lead to the generation of intermediates, which may adsorb on the surface of the catalyst. Slow diffusion of the generated intermediates from the catalyst surface can result in the deactivation of active sites on the photocatalyst and result in a reduction in the degradation rate. In contrast, at low concentration, the number of catalytic sites will not be limiting factor and the rate of degradation will be proportional to the substrate concentration, in accordance with apparent first-order kinetics (Hermann 1999). Priya and Madras 2006 examined the effect of initial concentration (10-76ppm) on the photocatalytic degradation of 2,4-dinitrophenol in the presence of combustion synthesized TiO₂ and P-25. The highest degradation was observed at 76ppm. Similar trends have been reported for the photocatalytic degradation of acephate (Rahman et al.2006), 2,4-DNP (Vora et al.2009), isoproturon (Haque and Muneer 2003), diphenamid (Rahman et al.2003) and propachlor (Muneer et al.2005). This is in accordance with the Langmuir-Hinshelwood (L-H) law. Several investigations have described the dependence of the photocatalytic degradation rates on the concentration of various phenols and dyes using the L-H kinetics model (Mathews 1988, 1990; Mills and Morris 1993). The L-H model is used to describe the dependence of the observed reaction rate on the initial solute concentrations (Turchi and Ollis 1990).

3.5 Catalyst loading

A number studies have indicated that the photocatlytic degradation rate initially increased with catalyst loading and then decreases at high values because of light scattering and screening effects. The tendency toward agglomeration (particle-particle interaction) also increases at high solids concentration, resulting in

a reduction in catalyst surface area available for light absorption and hence a drop in the photocatalytic degradation rate. Although the number of active sites in solution will increase with catalyst loading, a point appears to be reached where light penetration is to be compromised because of excessive particle concentration. The trade off between these two opposing phenomena results in an optimum catalyst loading for the photocatalytic reaction ([Adesina 2004](#)). A further increase in catalyst loading beyond the optimum will result in non-uniform light intensity distribution, so that the reaction rate would indeed be lower with increased catalyst dosage. Table 3 shows the influence of catalyst loading on the photocatalytic degradation of various organic compounds.

Table 3 Influence of catalyst loading on the photocatalytic degradation of various pollutants

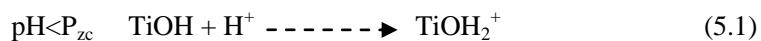
Pollutant	Light source	Photocatalyst	Catalyst dose range , g/L	Optimum dose, g/L	Ref.
Erioglaucine	UV	TiO ₂	0-0.35	0.3	Daneshvar et al.2006
Diazinon	UV	ZnO	0.5-4.0	3.0	Daneshvar et al.2007
Glyphosate	UV	TiO ₂	1.0-9.0	6.0	Shifu et al.2007
Thiram	Solar	TiO ₂	0-0.3	0.20	Kaneco et al.2009
Trichlorfon	UV	TiO ₂	5.0-10.0	8.0	Liu et al.2009
Phorate	UV	TiO ₂	0.1-1.0	0.5	Wu et al.2009
Tebuthioron	UV	TiO ₂	0.5-7.5	5.0	Muneer et al.2005
2,4,5 TCPAA	UV	TiO ₂	0.5-5.00	3.00	Singh et al.2007a
Phenol	UV/Visible	Fe ³⁺ -TiO ₂	0.4-1.0	0.5	Nahar et al.2006
2,4-dinitrophenol	UV	ZnO	1.0-3.0	3.0	Vora et al.2009
Propham	UV	TiO ₂	0.5-5.0	5.0	Muneer et al.2005
Terephthalic acid	UV	ZnO	0.2-3.0	2.5	Shafaei et al.2010
Beta-cypermethrin	UV	RuO ₂ -TiO ₂	2.0-6.0	5.0	Yao et al.2007
Methamodiphos	UV	Re-TiO ₂	2-12	1.0	Zhang et al.2009
Triclopyr	UV	TiO ₂	0.5-5.0	2.0	Qamar et al.2006
Methyl orange	Solar	SO ₄ ²⁻ -TiO ₂	0-2.5	2.5	Parida et al.2008
o-chlorophenol	UV	ZnO	1.0-3.0	2.0	Lathasree et al.2004
Picloram	UV	TiO ₂	0.2-2.0	2.0	Rahman and Muneer 2005
Floumeturon	UV	TiO ₂	0.5-3.0	3.0	Rahman and Muneer 2005
Carbofuran	UV	TiO ₂	0.025-0.125	0.1	Mahalakshmi et al.2007
Turbophos	UV	TiO ₂	0.1-2.0	0.5	Wu et al.2009
Carbendazim	UV	TiO ₂	0-0.09	0.07	Saien and Khezrianjoo 2008
Imazapyr	UV	TiO ₂	0.315-2.5	2.5	Pizarro et al.2005
Resorcinol	Solar	ZnO	0.5-3.5	2.5	Pardehs and Patil 2009

Singh et al.2007a examined the effect of catalyst concentration using three different TiO₂ powders on the degradation of phenoxy acetic acid (PAA) and 2,4,5-trichlorophenoxy acetic acid(2,4,5-TCPAA). P-25 was reported to be more efficient as compared to other TiO₂ powders at all the employed concentrations for the degradation of PAA and the order of efficiency was P-25>UV100>PC500. The degradation rate was shown to increase with the increase in catalyst loading up to 1g/L and, on further increase in catalyst loading, the degradation rate lead to a decrease for all catalysts. Similar trends were also observed for the degradation of 2,4,5-TCPAA and pyridaben as well as photocatalytic degradation of thiram.Under the conditions tested, Garcia and Takashima 2003 observed an optimum TiO₂ concentration of 8g/L for the degradation of imazaquin. The degradation rate was found to increase with increasing catalyst concentration up to 3 g/L and on subsequent addition of catalyst leads to the leveling off of the degradation rate. Similar results have been reported for photocatalytic degradation of thiram (Kaneco et al.2009), tebuthiron (Muneer et al.2005), Atrazine (Bahena et al.2008). Using ZnO and solar light, the photocatalytic degradation rate of 4-Nitrophenol (4-NP) was observed to increase upto 0.6g/L and then levelled off as the ZnO concentration increases to 0.8g/L (Parida et al.2006). An optimum concentration of P-25 was reported to be 0.1g/L under the conditions examined for the photocatalytic degradation of prometryrin (Evgenidou et al.2007).Wei et al.2009 indicated that the degradation of methamidophos increases with catalyst concentration from 2.0 to12.0g/L and further increase in TiO₂ results in reduced degradation. An increase in the amount of catalyst provides an increased number of active sites for adsorption; however, the simultaneous increase in the solution opacity inhibits the penetration of the photon flux. Kue et al.2010 observed that under visible light (400nm) irradiation, the photocatalytic degradation rate constants of BPA were 0.44 and 1.89 h⁻¹ for 0.5 g/L and 2 g/L TiO₂, respectively. However, further addition of TiO₂ (\approx 3.0 g/L) was reported to result in reduced degradation due to reduced visible light penetration. Under the conditions investigated, the optimum concentrations of TiO₂ and ZnO were found to be 3 g/L and 4 g/L respectively for efficient removal of 4-fluorophenol (Selvam et al.2007). In the presence of solar light, the highest photocatalytic degradation of phenol was observed at 2.5g/l of ZnO (Pardeshi and Patil 2008). In the presence of ZnO, Pardeshi and Patil 2009 tested the effect of catalyst loading (0.5-3.5g/L)on the solar photocatalytic degradation of resorcinol. The degradation of resorcinol was shown to increase with increase in ZnO up to 2.5g/L, further increase in photocatalyst amount showed negative effect due to increased turbidity of the suspension. In the presence of B/Ce-codoped TiO₂, the optimum catalyst loaing was observed to be 4.26g/L for the photocatalytic degradation of dicofol, cyfluthrin and fenvalerate in visible light irradiation (Lifen et al.2009). Using C-doped TiO₂, Xiao et al.2008 demonstrated the effect of catalyst loading (0.5-4.0 g/L) on the solar photocatalytic degradation of methylene blue in the order 1.0>2.0>4>0.5 g/L. They related the reported lower degradation at high catalyst loading with high turbidity due to C-doped TiO₂ nanoparticles.Using 036 mol %Co-doped TiO₂, Barakat et al.2005 tested the effect of catalyst loading (0.005-0.03 g/L) on the photocatalytic degradation of 2-CP. The degradation reached a maximum value of 93.4% with catalyst dosage of 0.01g/L.A further increase in the catalyst dosage slightly decreased the degradation efficiency. This suggests that the amount of photocatalyst to be used should

maintain a balance between these two opposing effects. In order to ensure efficient absorption of photons and to avoid excess catalyst, photocatalytic reactor should be operated at optimum catalyst loading.

3.6 Medium pH

Characteristics of organic pollutants in wastewater differ greatly in several parameters, particularly in their speciation behaviour, solubility in water and hydrophobicity. While some compounds are uncharged at common pH conditions typical of natural water or wastewater, other compounds exhibit a wide variation in speciation (or charge) and physico-chemical properties. At pH below its pKa value, an organic compound exists as neutral state. Above this pKa value, organic compound attains a negative charge. Some compounds can exist in positive, neutral, and negative forms in aqueous solution. This variation can also significantly influence their photocatalytic degradation behaviour. Wastewater pH varies significantly and can play an important role in the photocatalytic degradation of organic contaminants since it determines the surface charge of the photocatalyst and the size of aggregates it forms ([Bahnemann et al.2007; Haque et al.2006; Qamar et al.2006; Singh et al.2007a; Rahman et al.2006](#)) . The surface charge of photocatalyst and the ionization or speciation (pKa) of an organic pollutant can be profoundly affected by the solution pH. Electrostatic interaction between semiconductor surface, solvent molecules, substrate and charged radicals formed during photocatalytic oxidation strongly depends on the solution pH. In addition protonation and deprotonation of the organic pollutants can take place depending on the solution pH. Sometimes protonated products are more stable under UV-radiation than its main structures ([Saien and Khezrianjoo 2008](#)). Therefore the pH of the solution can play a key role in the adsorption and photocatalytic oxidation of pollutants. The ionization state of the surface of the photocatalyst can also be protonated and deprotonated under acidic and alkaline conditions respectively as shown in the following reactions:



The point of zero charge (P_{zc}) of the TiO_2 (Degussa P-25) is widely investigated/ reported at pH~6.25 ([Zhu et al.2005](#)). While under acidic conditions the positive charge of the TiO_2 surface increases as the pH decreases (Eq.5.1); above pH 6.25 the negative charge at the surface of the TiO_2 increases with increasing pH. Moreover, the pH of the solution affects the formation of hydroxyl radicals by the reaction between hydroxide ions and photo-induced holes on the TiO_2 surface. The positive holes are considered as the major oxidation steps at low pH, whereas hydroxyl radicals are considered as the predominant species at neutral or high pH levels ([Shifu and Gengyu 2005; Mathews 1986](#)). It would be expected that the generation of $\cdot\text{OH}$ are higher due to the presence of more available hydroxyl ions on the TiO_2 surface. Thus the degradation efficiency of the process will be logically enhanced at high pH. To elucidate the effect of pH on the photocatalytic degradation of organic compounds and adsorption on the TiO_2 surface, numerous investigations ([Singh et al.2007a,2007b,2007c, Rahman and Muneer 2005, Qamar and Muneer 2005, Muneer and Bahnemann 2002](#)) have been carried out. The degree of electrostatic attraction or

repulsion between the photocatalyst's surface and the ionic forms of organic molecule can vary with the change in solution pH, which can result in enhancement or inhibition on the degradation of organic pollutants in the presence of TiO₂. Table 4 shows the effect of pH on the photocatalytic degradation of various organic compounds. Wu et al.2009 indicated that degradation rate of turbuphos (neutral solute) decreased with a decrease in pH, and it proceeded much faster under alkaline pH. The observed behaviour is ascribed to the hydroxylation of catalyst surface due to the abundance of OH⁻ ions in alkaline conditions. Similar observation has also been made for the degradation of methamidophos (Wei et al.2009), carbofuran (Mahalakshmi et al.2007) and thiram (Kaneco et al.2009). However, the degradation rate of methamidophos was nearly independent of solution pH when Re-doped TiO₂ was used as the photocatalyst (Zhang et al.2009).

Table 4 Influence of pH on the photocatalytic degradation of various pollutants

Pollutant	Light source	Photocatalyst	Tested pH range	Optimum pH	Ref.
Atrazine	Solar	TiO ₂	2.0-9.99	4-5	Para et al.2004
Diazinon	UV	ZnO	3.5-11.3	5.2	Daneshvar et al.2007
Erioglaucine	UV	TiO ₂	2.4-12.2	2.4	Daneshvar et al.2006
Phorate	UV	TiO ₂	4.0-8.0	8.0	Wu et al.2009
Dimethoate	UV	TiO ₂	2.04-11.05	11.05	Chen et al.2007
Propham	UV	TiO ₂	3.0-11.0	5.0	Muneer et al.2007
2,4-DCP	Visible	N-TiO ₂	5.14-9.01	5.87	Xing et al.2009
Turbophos	UV	TiO ₂	3.0-8.0	8.0	Wu et al.2009
Beta-cypermethrin	UV	RuO ₂ -TiO ₂	2.4-10.8	6.42	Yao et al.2007
Terephthalic acid	UV	ZnO	8.0-11.0	9.0	Shafaei et al.2010
Propachlor	UV	TiO ₂	3.0-11.0	3.0	Muneer et al.2005
Methamidophos	UV	Re-TiO ₂	4.0-10.0	6.0	Zhang et al.2009
4-chlorophenol	UV	WO ₃ -TiO ₂	4.0-10.	4.0	Lin et al.2008
Methylparathion	UV-A	Bi ³⁺ -TiO ₂	2.0-10.0	2.0	Rengaraj et al.2005
Thiram	Solar	TiO ₂	2.5-11.4	8.0	Kaneco et al.2009
Isoproturon	Solar	TiO ₂	3.0-10.0	7.0	Sharma et al.2009
o-cresol	Visible	Pt-TiO ₂	3.0-11.0	9.0	Chen et al.2007
2,4-dinitrophenol	UV	ZnO	2.0-8.0	6.0	Vora et al.2009
4-CPAA	UV	TiO ₂	3.0-9.0	3.0	Singh et al.2007b
Carbofuran	UV	TiO ₂	4.0-9.0	7.0	Mahalakshmi et al.2007
Carbendazim	UV	TiO ₂	3.0-9.0	9.0	Saien and Khezrianjoo2008
Monocrotophos	UV	La-ZnO	8.0-10.0	10.0	Anandan et al.2007
Resorcinol	Solar	ZnO	4.0-10.	9.0	Pardeshi and Patil2009

A significant variation in the degradation of carbendazim ($pK_a=4.5$) has been shown in the pH range of 3-4.5 compared to 7-9 (Saien and Khezrianjoo 2008). In contrast, acidic or alkaline medium favours the degradation of glyphosate (Shifu et al.2007), and chlorphenapyr (Cao et al.2005). A decreasing trend has been observed for the photocatalytic degradation of PAA and 2,4,5-TCPAA in the pH range 3-9 (Singh et al.2007a). The degradation of imazaquin was also shown to decrease in the pH range 3-11(Garcia and Takashima 2003). The observed trends were attributed to the unfavourable electrostatic repulsion between the negatively charged surface of the catalyst and OH^- which decreases the degradation efficiency at higher pH (Qamar et al.2006). The higher degradation rate of diuron (Sayeh et al.2007), prophan and prophachlor (Muneer et al.2005) was observed at pH values 3-5, whereas the degradation rate was moderately influenced by the solution pH and increased slightly at pH 11.Under the conditions tested, Zhu et al.2005 reported a significant increase in the degradation rate of pyridaben at pH below 4. However, the degradation rate constant decreases gradually upon increasing pH from 6 to 11. Alkaline medium favours the the photocatalytic degradation of trichlorfon (Liu et al.2009). The photocatalytic degradation of metamitron in ZnO suspension was higher in acidic conditions compared to alkaline conditions (Minjin et al.2009). Under visible light irradiation, Xing et al.2009 studied the photocatalytic degradation of 100 mg/L 2,4-dichlorophenol(2,4-DCP) using P-25, TiO_2 and N- TiO_2 prepared in different conditions for a pH range 5.14-9.01. Compared to pure TiO_2 and P-25, the photocatalytic activities of N- TiO_2 are reported to be significantly higher for all the tested pH values. As the pH increases, the photocatalytic activity also increases at first and then decreases. The highest degradation was observed at pH 5.87 when N/Ti ratio is 2.0 and $\text{H}_2\text{O}/\text{Ti}$ ratio is 1:76. Anandan et al. 2007 reported that the degradation rate of monocrotophos (MCP) was significantly favoured in alkaline pH (8-10) compared to acidic pH when La-doped ZnO was used as the photocatalyst. Nonetheless, the degradation rate was reported to decline above pH 10 due to the neutral state of MCP. Lin et al.2006 indicated that the degradation rates of pentachlorophenol (PCP) using four metal(Au, Ag, Cu, Pt) doped- TiO_2 are shown to be higher at pH 3 than that obtained at pH 7. At pH 3, the degradation efficiency of four metal-doped TiO_2 is shown to follow the order: Au >Ag >Pt > Cu. In acidic solution, the positive surface charge of TiO_2 strongly attracted the negatively charged PCP since its pK_a value is at pH 4.74. This leads to an increase in its degradation.

Using 1%Au- TiO_2 prepared by photoreduction method, Iliev et al.2007 tested the influence of Au loading pH on the photocatalytic destruction of oxalic acid. The photonic efficiency was shown to increase from 0.79 to 1.87% with increasing pH from 3 to 7 and then it decreases to 1.67% as the pH increases to 9. For all the pH values (3-9) tested, the BET surface area is shown to decrease from 18 to $4 \text{ m}^2/\text{g}$ and the average particle size is observed to be decreased from 18 to 4 nm. Under visible light ($\lambda=410\text{nm}$) irradiation, the photocatalytic degradation rate constants of BPA at pH 4, 7 and 10 were shown to be 0.44, 0.31 and 0.10 h^{-1} , respectively (Kuo et al.2010). Since the pK_a value of BPA is 9.6–10.2, the electrostatic interactions between the TiO_2 surface and BPA resulted in higher adsorption and degradation at pH 4.0. In the presence of 0-1.5wt% Pt deposited TiO_2 and visible light irradiation, Chen et al.2007 noticed that the degradation of

o-cresol increases as pH value increases from 3 to 9. Furhther increase in pH to 10, results in a decrease in the degradation rate due to increased repulsion between TiO₂ surface and *o*-cresol which reduces adsorption of *o*-cresol on TiO₂. Venkatachalam et al.2007a indicated that the photocatalytic degradation of 4-CP was higher at pH 5 compared to alkaline pH. The reported higher degradation in the acidic pH is related to the enhanced adsorption of 4-CP on the TiO₂ surface. In the acidic pH, minimization of electron-hole recombination is an important factor for the enhanced degradation of 4-CP. The photocatalytic degradation of 4-NP was reported to increase 92% at pH 6.0 and then decreased with increasing pH until 7 (Parida et al.2006). This was related to negative charges of ZnO surface which hinders the degradation of 4-NP at pH 7. Using sulphate-modified TiO₂, the influence of pH on the photocatalytic degradation of methyl orange (MO) was reported to be pH 2>pH 4>pH6 >pH 8 in visible light (Parida et al.2008). Using C-doped TiO₂, the effect of pH (3-10) on the solar photocatalytic degradation and adsorption of methylene blue was demonstrated to be pH10>pH7>pH3 (Xiao et al.2008). Using 0.036 mol %Co-doped TiO₂, the effect of pH (4-12) on the photocatalytic degradation of 2-CP was shown to be pH12>pH11>pH9>pH7>pH4 (Barakat et al.2005). In the presence of TiO₂ and ZnO, the influence pH on the photocatalytic degradation of 4-fluorophenol was observed to be pH7>pH9>pH4 (Selvam et al.2007). The results summarized here indicate that a suitable pH control strategies should be implemented for an efficient photocatalytic water purification process.

3.7 Interfering substances

Since wastewater composition can vary with time, the basic understanding of the effect of organic and inorganic constituents present in wastewater on the performance of photocatalytic system is crucial to ensure operational stability of a prototype photocatalytic water purification process. A number of studies demonstrated that water components like calcium, magnesium, iron, zinc, copper, bicarbonate, phosphate, nitrate, sulfate, chloride, and dissolved organic matters can affect the photocatalytic degradation rate of organic pollutants since they can be adsorbed onto the surface of TiO₂ (Abdullah et al.1990,Parent et al.1996). Depending on the solution pH, they can also compete with the target pollutant for the active sites. The adsorption of water components can reduce the formation of •OH radicals. Although hydroxyl radical scavenging by the anions bicarbonate, phosphate, nitrate, sulfate, and chloride resulted in corresponding anion radicals, they have lower oxidation potential. Consequently all these reactions can influence the overall rate of photocatalytic oxidation. In order to elucidate the UV shielding effect from water turbidity, Giri et al.2010 tested the influence of inorganic solids (kaolin, bentonite and silica gel) on the photocatalytic degradation of 2,4-dichlorophenoxy acetic acid (2,4-D) using TiO₂ fiber module for a range from 0 to 1.0 g/l. In the absence of solids, 2,4-D removals due to photocatalytic oxidation are shown to be about 53% after 2h reaction. However, the removals were reported to decrease the lowest values (~41%, 14% and 38%) for 3.0g/L kaolin, 0.5g/L bentonite and 0.5g/L silica gel in the same period. The apparent zero order reaction rate also showed the strong inverse correlation between solid concentration (0-0.5g/l) and 24-D removal in case of bentonite and silica gel, nonetheless, this was not observed for kaolin particles.

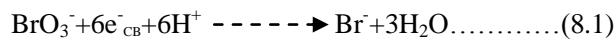
Chen et al.2010 examined the effect of humic acid (HA) (0 to 25mg/l) as possible photosenitizer on the photocatalytic mineralization of dimethoate. Upon 60 min irradiation, the mineralization efficiency is shown to increase from 63.73 % and 78.88% as the HA concentration increases from 0 to 5mg/L. Further increase in HA led to a decrease in photocatalytic efficiency. This was attributed to the reduced light transmittance due to the excessive HA in reactive solution and the competitive adsorption of HA for the active sites on the catalyst surface. They also tested the effect of CH_3COCH_3 concentration (0 to 1.0 % (v/v) on the dimethoate mineralization at neutral pH. The mineralization rate appears to decrease from 36.73 to 9.23% with increasing CH_3COCH_3 concentration due to the competition of dimethoate for the reactive site. Under the conditions examined, the influence of Fe^{3+} , Cu^{2+} , Zn^{2+} , HCO_3^- and NO_3^- on the extent of mineralization is shown to increase with increasing ions concentration and reached a maximum level at optimal concentrations. In contrast, the mineralization of dimethoate was observed to be strongly inhibited by Cl^- and Cr^{3+} ions. Rabindranath et al.2003 studied the effect of Cl^- , PO_4^{3-} , and NO_3^- on the photocatalytic degradation of phosphamidon. In the presence of 1.5×10^{-4} M of the tested anions, no significant effect was observed under the conditions examined. However, the degradation rate was reported to be inhibited by these anions at high concentration which was attributed to the competition of ions for active sites on the TiO_2 surface. The order of inhibition of three anions on the degradation rate is shown as $\text{PO}_4^{3-} > \text{Cl}^- > \text{NO}_3^-$. Shifu et al.2007 tested the effect of SO_4^{2-} , Cl^- , Br^- , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Zn^{2+} , Co^{2+} and Ni^{2+} on the photocatalytic degradation rate of glyphosphate. No discernible effect was observed when trace amount of these anions were added to the solution. The degradation of glyphosate was reported to increase with the addition of 0.05mM Fe^{3+} and 0.01mM Cu^{2+} in solution. The scavenging of electrons by metal ions and subsequently preventing the recombination of electron-hole pairs, favours the formation of $\cdot\text{OH}$ and O_2^{2-} on the TiO_2 surface. In the presence of SO_4^{2-} , Cl^- , Br^- , Fe^{3+} and Cu^{2+} , similar results have been observed for the degradation of methamidophos (Wei et al.2009).

Shifu et al.2005 examined the effect of Cu^{2+} , Zn^{2+} and Na^+ on the photocatalytic degradation of MCP and phorate. No discernible effect was observed with the addition of small amount of Zn^{2+} or Na^+ . However, the degradation efficiency of tested compounds are shown to increase when 0.05 mM/dm³ Cu^{2+} was added to the solution. Further Cu^{2+} addition results in reduced catalytic efficiency due to the predominance of $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$. In the presence of Cu^{2+} and Ni^{2+} ions (0.04-0.31 mM/L), the degradation efficiency of imazapyr was reported to decrease by factors of 4 and 2 for the cooper and nickel respectively (Carrier et al.2006). Mahmoodi et al.2007 investigated the effects of Cl^- , NO_3^- , and SO_4^{2-} on the photocatlytic degradation of diazinon and imidaclorpid respectively. The observed inhibitive effect on the degradation of the tested pollutants is shown to follow the order: $\text{SO}_4^{2-} < \text{NO}_3^- < \text{Cl}^-$. The detrimental effect of the tested anions is attributed to their competition for the active sites on the TiO_2 surface and catalyst deactivation which subsequently, decrease the degradation rate. A major drawback from the high reactivity and non-selectivity of $\cdot\text{OH}$ is that it also reacts with non-target compounds present in the background water matrix. This results in a higher $\cdot\text{OH}$ demand to accomplish the desired degree of degradation (Parent et al.1996). Wu et al.2009 examined the effect of nitrate and chloride anions on the photocatalytic degradation of turbophos and

phorate (Wu et al.2009). Significant inhibition on the degradation efficiency has been reported due to the presence of anions. As explained in several studies (Mahmoodi et al.2007, Wu et al.2009) that inhibition is due to the reaction of positive holes and hydroxyl radicals with anions that behaved as radical (h^+ and $\cdot OH$) scavenger resulted in longer turbophos removal. Mijin et al.2009 studied the effect of NaCl, Na_2CO_3 and Na_2SO_4 salts on the photocatalytic degradation of metamitron in ZnO suspension. The effects of salt addition are shown to be in the order: $CO_3^{2-} > SO_4^{2-} > Cl^-$. Negligible inhibition was observed when the concentration of NaCl was 20mM. Dissolved organic matter (DOM), ubiquitously present in storm and wastewater effluent also plays an important role in regard to pesticide degradation. Lin and Lin 2007 observed that the presence of humic acid caused a significant retardation on the photocatalytic degradation of 4-chlororphenol. The observed retardations of humic acids was related to the inhibition (surface deactivation), competition and light attenuation effects. Moreover the presence of humic acid in the reaction mixture has been reported to significantly reduce light transmittance, and therefore the photooxidation rate. Zhu et al.2005 examined the effect of water content(0-50%) on the initial reaction rates of photocatalytic degradation of pyridaben. The initial reaction rate were shown to follow the sequence: acetonitrile/ H_2O (80/20)>(90/10)>(70/30)> (60/40)>(95/5)>(50/50)>(100/0). This order was indicated to be related to hydroxyl radials generated and the solubility of pyridaben in various cases. Kundu et al.2005 studied the effects of various solvents on the photodegradation of 2,4-dichlororphenoxy acetic acid in 10% aqueous methanol and 10% aqueous acetonitrile. The photodegradation was also studied in two different micellar environments such as aqueous $10^{-2}M$ Cetyltrimethyl ammonium chloride (CTAC) micelle (cationic) and aqueous sodium dodecyl sulphate (SDS) anionic micelle ($10^{-2}M$). Under 45 min irradiation, the degradation was varied in the range of 16-57%. The degradation of 2, 4-D in the CTAC micelle was observed to be higher and it was more than two times as obtained with other conditions. The effect of transition metal ions on the degradation of 4-fluorophenol was shown to be in the order of $Mg^{2+} > Fe^{3+} > Fe^{2+} > Cu^{2+}$ and the inhibition of inorganic anions on the degradation of 4-FP was demonstrated to be $CO_3^{2-} > HCO_3^- > Cl^- > NO_3^- > SO_4^{2-}$ (Selvam et al.2007). Naeem et al.2008 reported that the order of anions inhibition on the photocatalytic degradation of phenol is $Cl^- > SO_4^{2-} > NO_3^- > CO_3^-$. At certain level, Fe^{3+} is reported to improve the degradation rate whereas Ca^{2+} , Cu^{2+} , and Mg^{2+} hinder the degradation process. The effect of surfactants (0.05mM/L) on the degradation rate was observed to be sodium dodecyl benzene sulphate (SDBS) > sodium dodecyl sulfonate (AS)>sodium dodecyl sulphate (SDS). The presence of anions is reported to alter the ionic strength of the solution, which influences the catalytic activity and the photocatalytic degradation. Marinas et al.2001 studied the influence of humic acids on the photocatalytic degradation of formetanate (FMT). In the presence of humic acid, the degradation rate was shown to decrease due to the competition between FMT and humic acids for active sites on the catalyst surface. The photocatalytic degradation of 2,4-dichlororphenoxy acetic acid and 4-chloro-2-methylphenoxy acetic acid was reported to be inhibited by 70% and 80% due to the presence of 1.4×10^{-2} mol/L ethanol (Djebbar et al.2006). Inorganic anions, such as phosphate, sulphate, nitrate, and chloride, have been reported to limit the performance of solar based photocatalysis (Parent et al.1996).

3.8 Oxidants/electron acceptor

The electron/hole recombination is one of the main drawbacks in the application of TiO₂ photocatalysis as it causes waste of energy. In the absence of suitable electron acceptor or donor, recombination step is predominant and thus it limits the quantum yield. Thus it is crucial to prevent the electron-hole recombination to ensure efficient photocatalysis. Molecular oxygen is generally used as an electron acceptor in heterogenous photocatalytic reactions. Addition of external oxidant/electron acceptors into a semiconductor suspension has been shown to improve the photocatalytic degradation of organic contaminants (1) by removing the electron-hole recombination by accepting the conduction band electron; (2) increasing the hydroxyl radical concentration and oxidation rate of intermediate compound; and (3) generating more radicals and other oxidizing species to accelerate the degradation efficiency of intermediate compounds ([Singh et al.2007a,2007b,2007c, Rahman and Muneer 2005a,2005b; Qamar and Muneer 2005, Muneer and Bahnemann 2002](#)). Since hydroxyl radicals appear to play an important role in the photocatlytic degradation, several researchers have investigated the effect of addition of electron acceptors such as H₂O₂, KBrO₃, and K₂S₂O₈ on the photocatlytic degradation of various pesticides and herbicides ([Bahnemann et al.2007,Singh et al.2003,2004; Rahman et al.2006, Wei et al.2009](#)) to enhance the formation of hydroxyl radicals as well as to inhibit the electron/hole (e⁻/h⁺) pair recombination. In all cases the addition of oxidants has resulted in higher pollutant degradation rate compared to the molecular oxygen. In most of the cases, the order of enhancement is UV/TiO₂/BrO₃>UV/TiO₂/S₂O₈²⁻>UV/TiO₂/H₂O₂. The enhancement of degradation rate is due to reaction between BrO₃⁻ and conduction band electron ([Singh et al.2007a, 2007b, 2007c; Rahman and Muneer 2005a, 2005b](#)). This reaction reduces the recombination of electron-hole pair.



$\text{S}_2\text{O}_8^{2-}$ can generate sulphate radical anion ($\text{SO}_4^{\bullet-}$) both thermally and photolytically in aqueous solution.

$\text{SO}_4^{\bullet-}$ then reacts with H_2O to produce $\cdot\text{OH}$ radicals.



With the addition of H_2O_2 , the enhancement of degradation is due to the increase in the hydroxyl radical concentration as shown by Eq. (8.4) and (8.5);



The degradation efficiency of UV/TiO₂/oxidant process is slightly more in acidic medium than in basic medium. Wei et al. 2009 examined the effect of H₂O₂, KBrO₃ and K₂S₂O₈ addition on the photocatalytic degradation of methamidophos by varying the amount of oxidant concentration. The optimum concentrations of the oxidants were 0.8mM/L, 4.0mM/L and 0.8mM/L for H₂O₂, KBrO₃ and K₂S₂O₈ respectively. Of the oxidants studied, K₂S₂O₈ was demonstrated to be most effective for the degradation of

methamidophos. KBrO₃ was shown to be more efficient acid as compared to H₂O₂ for improving the degradation rate of tebuthiuron, propachlor, chlortoluron, thiram (Bahnemann et al.2007), PAA and 2,4,5-TCPAA(Sing et al.2007a), terbacil and 2,4,5-tribromoimidazole (Muneer and Bahnemann 2002), imazapyr(Carrier et al.2006),dimethoate (Chen et al.2007) , Glyphosphate(Shifu et al.2007). The reduction of bromated 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, e.g. BrO₂⁻ and HOBr (Singh et al.2007a). Moreover, bromated ions by themselves can act as oxidizing agents. In contrast H₂O₂ was reported to be efficient for prophan, prophachlor (Muneer et al.2005)and triclopyr, daminozid (Qamar et al.2006), dicamba and floumeturon (Rahman and Muneer 2005). Both H₂O₂ and K₂S₂O₈ were shown to be equally effective for prometryn degradation at an optimum concentration of 2mM (Evgenidou et al.2007). However, the degradation rates were also demonstrated to decrease at high concentration. This behavior has been related to the modification of TiO₂ surface by H₂O₂ adsorption and scavenging of the photogenerated holes and reaction with hydroxyl radicals. The effect of oxidants on the degradation of 4-fluorophenol was shown to be in the order of IO₄⁻>BrO₃⁻>S₂O₈²⁻>H₂O₂> ClO₃⁻ (Selvam et al.2007). Park et al.2009 studied the effect of H₂O₂ concentration (from 0-3.0mM) on the photocatalytic degradation of benomyl.Under the conditions investigated (C₀=3.2mg/l, TiO₂=2.0g/l, I_{UV}=6.525mW/cm²), the degradation rate constant of benomyl are shown to vary from 0.0208 min⁻¹ to 0.0235 min⁻¹. Under the conditions tested, the effect of oxidant addition on the photocatalytic degradation of trichlorfon is shown to be in the order: K₂S₂O₈>KBrO₃>H₂O₂ (Liu et al.2009).This trend may be attributed to the generation of highly reactive intermediate radicals SO₄^{•-} from K₂S₂O₈ and oxidizing agents such as, BrO₂ and HOBr from KBrO₃etc.

3.9 Mode of application: Suspended vs immobilized system

The efficiency of suspended catalysts (TiO₂) has been demonstrated to be superior compared to the immobilized catalyst (Parent et al.1996). This can be attributed to the enhanced mass transport in suspended form. However, the cost incurred for catalyst recovery makes the slurry system impractical. In contrast, immobilized catalyst would be easier to handle but will likely be more costly due to fouling and deactivation of catalyst. The reasons for the deactivation include (a) generation of reaction by products which cause the loss of active sites on the surface, and (b) fouling which changes the catalyst surface by blocking pores. The stability and the photoreactivity of the catalyst are strongly influenced by the amount of hydroxyl groups. As the reaction proceeds, the density of hydroxyl groups on the catalyst surface decreases, consequently the activity of the catalyst drops. The experimental results (Dutta and Ray 2004) indicated that strongly adsorbed intermediates occupied the active sites on the catalyst surface and led to the loss of photocatalytic activity. Therefore, more efforts should be focused on to eliminate the intermediates that occupy the active sites of the catalyst and regenerate the hydroxyl radicals. Comparable photodegradation kinetics of atrazine has been obtained when TiO₂ was used in suspended and immobilized systems (Para et al.2004). Pizzaro et al.2005 evaluated the photocatalytic degradation of imazaphyr using powdered and supported catalytic system for titania P-25 and PC-500. In the case of

powdered titania, $76.5\mu\text{mol}\cdot\text{L}^{-1}$ of imazaphyr was completely degraded with P-25 after 30 min irradiation. In contrast, only 45% conversion of imazaphyr was achieved with PC-500. However, when a mixture of PC-500 and P-25 with a ratio 1:1 was used as the catalyst composition; imazaphyr disappeared practically at the same rate as the pure P-25. In the case of three supported catalysts, the conversions of same amount of imazaphyr after 4 hours irradiation were 82, 89 and 21.4% for P-25, P-25+PC-500 and PC-500 respectively. [Madani et al.2006](#) studied the photocatalytic degradation of diuron in the presence of paper-supported TiO_2 catalysts. Regardless of the nature of TiO_2 (P-25 or PC500 or their equimolar mixture deposited on paper NW 10), the photocatalytic degradation rate of diuron was similar to the results obtained with suspended powders. The efficiency of PC 500 deposited on NW10 paper was comparable to that obtained with unsupported PC 500. In contrast, P-25/NW10 showed two times lower efficiency compared to P-25 powder. Using supported and suspended TiO_2 , the degradation rate of chlortoluron was compared under identical (2.8g/L) TiO_2 loading and other experimental conditions ([Lhomme et al.2008](#)). TiO_2 supported on non-woven paper appeared to be an efficient photocatalyst for degrading and mineralizing chlortoluron. Photocatalytic degradation of methyl parathion, dichlorvos and lindane in aqueous medium were investigated with suspended and immobilized system ([Senthilnathan and Philip 2009](#)). The rate constant of methyl parathion and dichlorvos was reduced by 50% when the initial concentration increased by 10 times. In contrast, the rate constant of lindane was decreased by almost 30%. As the pesticide concentration increases, the adsorption of pesticide on the active sites of catalyst surface increases. Hence, competitive adsorption of OH^- for the same sites decreases, thus reducing the formation of $\cdot\text{OH}$. Under the conditions examined, at low concentration of pesticides, there was no significant variation in degradation rates obtained in suspended and immobilized TiO_2 systems. Recently, there has been growing interest for the development of photocatalyst supported on various materials e.g glass and alumina beads, zeolites ([Shankar et al.2006](#), [Sharma et al.2008a, 2008b](#)). [Sahnkar et al.2006](#) indicated that 1wt % TiO_2 supported on HY zeolite was reported to be efficient for the photocatalytic degradation of 2,4-dichlorophenoxyacetic acid compared to bare TiO_2 . This effect was associated with the improved adsorption and efficient delocalisation of photogenerated electrons by zeolite support. [Sharma et al.2008a](#) studied the photocatalytic degradation of isoproturon in a TiO_2 immobilized over mesoporous SBA-15 composite system using solar light. 10 wt% TiO_2 /SBA supported system was reported to show higher photocatalytic activity compared to bare TiO_2 . This was attributed to the synergistic effect resulted from the adsorption of isoproturon over mesoporous material facilitating the degradation. In addition to isoproturon, the composite was shown to be efficient for the degradation of imidaclorapid and phosphamidon in wastewater. Similar observations have been made for the degradation of isoproturon in a 10wt% TiO_2 supported on Al-MCM-41 composite ([Sharma et al.2008b](#)). This was related to the delocalization of electrons which come from TiO_2 excitation and inhibits electron and hole recombination. The dispersion of TiO_2 over mesoporous materials to eliminate particle-particle aggregation and light scattering by TiO_2 , which provides complete harvesting of solar light. [Zhao et al.2009a](#) reported the enhanced degradation efficiency for a composite TiO_2 supported on NaY zeolite (Specific surface area=659 m^2/g , particle size=0.65nm) for the degradation of omethoate under the optimal conditions. A

composite of 5wt % TiO₂ and porous nano silica was reported to be efficient compared to TiO₂ for the degradation of imidaclorpid and phosphamidon in wastewater ([Sharma et al.2009](#)).

3.10 Synthesis technique and Calcination temperature

A range of techniques have been employed to prepare nanocrystalline TiO₂ powder for catalytic purposes including sol-gel method, solvo-thermal process, reverse micellar, hydrothermal method and electrochemical methods. Of these methods, sol-gel process is regarded as promising alternatives due to its low sintering temperature, versatility of processing and homogeneity at molecular level. The structure and size of TiO₂ crystallites significantly depends on calcination temperature. Thermal treatment of TiO₂ gels at higher temperature promotes phase transformation from thermodynamically metastable anatase to more stable and condensed rutile phase. As dehydration occurs during heat treatment, crystallites grow to dimensions larger than those of the original particles. [Table 5](#) shows the influence of calcination temperature on photocatalytic degradation of various organic contaminants. Using ZnO thin films, [Aal et al. 2009](#) examined the effect of calcination temperature(350-550°C) and time (1-2h) on the photocatalytic degradation of 2,4,6-trichlorophenol. The growth of ZnO nano-structure was found to be dependent on calcinations time and temperature. Optimum ZnO nano-fibres is observed to be formed uniformly after 2h oxidation at 550°C. [Zhao et al.2009](#) showed that the optimum temperature for the photocatalytic degradation of omethoate was found to be 550°C. Under the conditions investigated, a sharp decrease in the degradation rate at 650°C has been related to the over growth of the TiO₂ crystal size and the presence of a rutile phase in the TiO₂ crystal. [Amadelli et al.2008](#) tested the effect of calcination temperature (100-500°C) on the time required for mineralization of 4-CP using 0.2%Co-TiO₂ (prepared by the incipient impregnation method) and TiO₂. The best result was obtained for the sample calcined at 400°C for 30 minutes; however, heating over 2h at this temperature did not result in any appreciable changes in surface area and anatase/rutile phase ratio. Co-TiO₂ is shown to be more active than the pure TiO₂ for all treatment temperatures. [Song et al.2009](#) investigated the effect of titania films with different nanostructures of nanorods (NR), sol-gel film(SG), nanotubes (NT) and nanoparticle aggregates on the photocatalytic degradation of rodamine B (RB) , methylene blue(MB) and methyl orange(MO). In the case of RB degradation, the observed order was reported to be NR>DP>SG>NT, while the order was shown to be NR>SG>DP>NT for the degradation of MB. However an order of NT>DP>SG>NR was found for the degradation of MO. Using 0.50wt% Pt-TiO₂, [Chen et al.2007](#) tested the effect of calcination temperature (150-750°C) on the photocatalytic degradation of o-cresol under visible light. The reaction rate constant was reported to decrease as the calcination temperature increases from 150 to 750°C. This was related to the decrease in surface area as the calcination temperature increases for the above range.Using C-doped TiO₂, the complete solar photocatalytic degradation of MB (Co=10mg/L) was observed at 600°C in 80 min irradiation due to stronger absorption of the C-doped TiO₂ in 300-500nm range([Xiao et al.2008](#)). [Pardeshi and Patil 2009](#) tested the effect of calcination temperature (400-900°C) on the solar photocatalytic degradation of resorcinol using ZnO. ZnO calcined from 400°C to 550°C showed about 100% degradation with in 7h even if the ZnO particle size increases from 31.8nm to 51.9 nm. This was related to the uniform

ZnO crystallite growth rate up to 550°C, which gives ZnO of same morphology. After 550°C the degradation efficiency was observed to decrease with increase in calcinations temperature. This may be due to the increase in ZnO crystallite size with calcinations temperature which leads to a decrease in number of active sites of photocatalyst for adsorption of substrate molecules. Using C-doped TiO₂ prepared by sol-gel method, Park et al.2009 tested the effect of calcination temperature (100-500°C) on the photocatalytic degradation of 4-CP under visible light ($\lambda > 420\text{nm}$) irradiation. Maximum degradation was obtained at 250°C. Further increase in calcination temperature above 300°C results in a dramatic fall in the visible light activity, indicating that the incorporation of the lattice carbons is hindered at higher temperatures.

Table 5 Influence of calcinations temperature on the photocatalytic degradation of various pollutants

Pollutant	Light source	Photocatalyst	Range of calcination	Optimum calcination temperature	Ref.
Omethoate	UV	TiO ₂	350-650°C	550°C	Zhao et al.2009b
Beta-cypermethrin	UV	RuO ₂ -TiO ₂	400-700°C	500°C	Yao et al.2007
Methamidophos	UV	Re-TiO ₂	400-800°C	700°C	Zhang et al.2009
4-chlorophenol	Visible	C-TiO ₂	100-500°C	250°C	Parrk et al.2009
4-chlorophenol	Visible	Co-TiO ₂	100-500°C	400°C	Amadelli et al.2008
o-cresol	Visible	Pt- TiO ₂	150-750°C	150°C	Chen et al.2007
Phenol	UV	TiO ₂	400-900°C	800°C	Tian et al.2009
Methylene blue	UV	C-TiO ₂	500-800°C	600°C	Xiao et al.2008
Phenanthrene	Visible	N-TiO ₂	400-700°C	400°C	Sirisaksoontorn et al.2009
4-chlorophenol	UV	Zr ⁴⁺ -TiO ₂	105-1100°C	900°C	Lukac et al.2007
Rhodamine B	Solar	TiO ₂	300-800°C	700°C	Wang et al.2008
Phenol	UV/Visible	I-TiO ₂	400-600°C	400°C	Hong et al.2005
Phenol	Visible	N-TiO ₂	350-500°C	400°C	Wang et al.2005
2,4,6-TCP	UV	ZnO	350-550°C	550°C	Aal et al.2009
Resorcinol	Solar	ZnO	400-900°C	550°C	Pardeshi and Patil 2009

Sirisaksoontorn et al.2009 studied the efficacy of N-doped TiO₂ for the degradation of phenanthrene under visible light. Using the N-doped TiO₂ (size=8.84nm, BET= 253.7m²/g) calcined at 400°C; nearly 80% degradation was observed in 8h irradiation. In contrast, less than 10% degradation was obtained using either N-doped TiO₂ (BET=74m²/g) calcined at 500°C or P25 (49.2m²/g). The higher activity of the N-doped TiO₂ calcined at 400°C was attributed to its smaller particle size and the greater number of active sites due to larger surface area. The N-doped TiO₂ showed the anatase-to-rutile phase transformation at calcination temperature range of 400–700°C. Wang et al.2005 investigated the effect of calcination temperature (350-500°C) on the photocatalytic activity of N-doped TiO₂ for the degradation of phenol in visible ($\lambda > 400\text{nm}$) light. The amount of mineralization was reported to be 24.1% at 350°C and 35.6% at 400°C in 120min respectively. In contrast, N-doped TiO₂ calcined at 500°C and P25 did not significantly change the total organic carbon value. The high photocatalytic activity at 400°C is partially due to the

smaller particle size and higher adsorption area toward the organic substrate as well as the intense absorption in the visible light range and a red shift in the band gap transition of the doped TiO₂ samples. Tian et al.2009 tested the effect of calcination temperature (400-900°C) on the photocatalytic activity of biphasic TiO₂ synthesized by hydrothermal process and ammonia post treatment for the degradation of phenol (50mg/L). Under the conditions examined, the sample calcined at 800°C showed the highest activity due to large surface area, high crystallinity and separation rate of charged carriers, and heterojunction microstructure between anatase and brookite. The sample calcined at 900°C showed reduced activity due to the excessive decrease of surface area and the growth of sample particles. Using the Re-doped and undoped TiO₂, Zhang et al.2009 studied the effect of calcination temperature on the degradation of methamidophos. For both catalysts, the degradation efficiency was shown to increase for the calcination temperature from 400°C to 600°C. This effect was ascribed to the growth of crystallization and the elimination of photocatalyst amorphism due to temperature increment. However, the degradation efficiency was reported to decrease with further increase in temperature (>600°C) due to crystal development. Doped nano-TiO₂ was reported to have better photocatalytic activities until 700°C due to the presence of Re and the resulting inhibition on crystal growth. Bessekhouad et al.2004 studied the effect of alkaline (Li, Na, K) doped TiO₂ prepared by sol-gel route and impregnation method on the photocatalytic degradation of benzamide. The crystallinity levels of catalysts are found to be largely dependent on both the nature and the concentration of alkaline. The best crystallinity is obtained for Li-doped TiO₂ and is lowest for K-doped TiO₂. For a given alkaline concentration, the catalyst prepared by the impregnation technique was shown to be more efficient than those prepared by sol-gel route. The half life of benzamide was two to four times higher compared to undoped TiO₂. The half-life of benzamide obtained with 5% Li-doped TiO₂ was comparable to P-25. The half-life of benzamide with 1% K-doped TiO₂ was shown to be lower than that of P-25. 1% Na-doped TiO₂ prepared by impregnation method is reported to better than P-25. Using hydrothermal assistant sol-gel method, An et al.2008 tested the effect of the calcination temperatures (350-650°C) on the photocatalytic activity of mesoporous TiO₂ for the degradation of 2,4,6-tribromophenol (TBP). XRD analysis indicated that a sample calcined at 350°C possesses a high BET surface area of 142 m²/g and the observed BET surface area was reduced to 49m²/g when the calcinations temperature was increased to 550°C. The BET surface area was 7m²/g when the sample calcinated at 650°C, which was attributed to the complete, collapsed mesoporous structure. In addition, the degradation of 2,4,6-TBP was reported to increase as the calcination temperature increases from 350 to 550°C and then sharply decrease when the sample calcination temperature further rises to 650°C. This was due to the increase in crystalline size from 9.8 to 18.4 nm and the resulting decrease in BET surface area from 142 to 49 m²/g and completely collapsed mesoporous structure at 650°C. Gorska et al.2009 tested the influence of calcinations temperature (350°C-750°C) on the photocatalytic degradation of 0.21mM phenol under UV (250<λ<400nm) and visible (λ>400nm) light irradiation. Using P-25 sample calcined at 350°C, the highest amount of phenol degradation was shown to be 80% in 60 min in the visible light. In addition to the largest BET surface area (205.8m²/g) and the smallest crystallite size(8.4nm) and average pore diameter(8.3nm) of TiO₂, this effect was attributed to the efficient absorption of light vis region due to the existence of

largest amount of carbon in aromatic C-C bonds (10.1 at%). In contrast, the photocatalyst calcinated at 450°C was reported to have the highest activity in UV light. Under visible light irradiation, Wawrzyniak et al.2006 studied the effect of calcinations temperature (100-800°C) on the photocatalytic degradation of phenol and two azo dyes (reactive Red, direct Green) by N doped-TiO₂. The highest amount of phenol was degraded at 700°C. For the degradation of both azo dyes, the highest degradation was achieved at 500°C and 600°C respectively. Using N-doped TiO₂ and visible light, the maximum amount of phenol degradation was achieved at 600°C and no variation was observed at 700°C and 800°C (Silveyra et al.2005). Lettman et al.2001 observed that about 30% 4-CP(C₀=0.25mM) was degraded after 100 min irradiation($\lambda>400$) in using a catalyst obtained by hydrolysis, followed by calicnation at 250°C for 3h. Using a carbon doped TiO₂ prepared by TiCl₄ hydrolysis in tetrabutylammonium hydroioxide (calcination at 400°C, 1h), 70 % TOC reduction of 0.25mM 4-CP was reported by Shaktivel et al.2004. The highest photocatalytic degradation of phenol using 2%-Au/TiO₂ was observed at 275°C in solar light (Sonawane and Dongare2006). Using ZnO upon solar irradiation, the photocatalytic degradation of 4-NP increases from 52.9 % to 74.4% as the calcination temperature increases from 110 to 300°C due to higher surface area and lower crystallite sizes (Parida et al.2006). Under visible light irradiation, Gorska et al.2009 reported that about 60% phenol was degraded after 60 min in the presence of C-doped TiO₂ calcined at 350°C. Under visible light, Li and Liu 2008 examined the photocatalytic activity of N-F codoped TiO₂ prepared by acid catalysed hydrolysis for the degradation of phenol over a range of calcination temperature 600-900°C. The sample with 1:0.1 ratio of TiO₂ to NH4F showed maximum degradation at 700°C and the complete degradation is shown to achieve within 60 min whereas only 15.5% and 13.0% phenol were degraded with pure TiO₂ and P-25 in 100 min. The activity of N-F codoped TiO₂ was also higher than the bare TiO₂ and P-25 in UV light. N-F codoping can improve dispersion of TiO₂ by inhibit particle size agglomeration, and retard phase transformation. Lukac et al.2007 examined the effect of annealing temperature (105-1100°C) on the photocatalytic activity of Zr-doped TiO₂ for the degradation of 4-chlorophenol. The samples annealed between 800 and 900°C are more efficient than the standard photocatalyst P-25. The optimum size of the Zr doped anatase crystallites is 69.2 and 86.5 nm obtained at 875 and 900°C, respectively. The photocatalyst annealed at 900°C was reported to have 1.5 times higher degradation rate compared to P-25. At 900°C, the sample is shown to have 87 wt.% of anatase and 13 wt.% of rutile. Using I-doped TiO₂ with anatase phase, Hong et al.2005 investigated the effect of calcination temperature (400-600°C) on the photocatalytic degradation of phenol under UV and visible light irradiation ($\lambda>400nm$). Of the temperatures tested, I-doped TiO₂ calcined at 400°C shows significantly higher photocatalytic activity compared to undoped TiO₂ nanoparticles (P-25 and pure TiO₂). Using N-F codoped TiO₂ prepared by sol-gel approach Meng et al.2009 tested the effect of calcination temperature (400-700°C) on the photocatalytic degradation of methylene blue in visible light (>410nm) irradiation. The sample (BET=42 m²/g) calcined at 500°C showed better photocatalytic efficiency. The phase transformation from anatse to rutile was hindered due to codoping with N and F.

3.11 Doping and mixed semiconductor

The light that TiO_2 can utilize is limited to UV fraction of the entire solar spectrum. A number of approaches have been suggested to enhance the photocatalytic activity of TiO_2 in the visible light. Modification of TiO_2 surface is one of the promising routes to enable TiO_2 sensitive to visible light for its use in water purification. Metal ion doping and co-doping with non-metals can improve trapping of the photo excited conduction band electrons at the surface whereby minimizing charge carrier recombination (Iwasaki et al.2000, Abramovic et al.2007,2009, Rockafellow et al.2009, Tryba2008, Dvoranova et al.2002, Sanchez and Lopez 1995, Kato et al.2005). Successful doping can result in enhanced efficacy of the photocatalyst system. Several dopants used e.g Sn (Freshno et al.2005) Ag and Pd (Liqiang et al.2006), Re (Zhang et al.2009), Bi^{3+} (Rengaraj et al.2005), $\text{V}^{5+},\text{Mo}^{6+}$ and Th^{4+} (Devi et al.2008,2009, Devi and Murthy2008), Pt^{6+} (Katsumata et al.2009) were shown to enhance photocatalytic activity substantially for the systems examined. However, the photoactivity of the metal-doped TiO_2 photocatalyst significantly depends on the dopant ion nature and concentration, preparation method and operating conditions (Dvoranova et al.2002). Both positive and negative results have been reported from doping with metal ions. It is desired that the deposition of metal ions on TiO_2 can modify the photoconductive properties by increasing the charge separation efficiency between electrons and holes, and also by acting as a trap for electrons, inhibiting volume and surface recombinations of electron and hole that reduce the photoefficiency of TiO_2 photocatalyst (Sanchez and Lopez 1995). The increase in charge separation efficiency will enhance the formation of both free hydroxyl radicals and active oxygen species (Kato et al.2005). In contrast, the photocatalytic activity of metal doping is impaired by thermal instability and the recombination of photogenerated electrons and holes (Borous et al.2007).The amounts of doping concentration along with a summary of the pesticides degraded using doped catalyst are shown in Table 6.

3.11.1 Influence of metal doping

Modification of TiO_2 through metals is increasingly being considered for maximizing its photocatalytic efficiency. The exerted effects depend on selected metal and content, type of TiO_2 used, nature of organic pollutants, and the photoreactor medium. Rengaraj et al.2005 reported that the highest degradation and mineralization of methylparathion was achieved in the doping range of 0.7-1.5% Bi^{3+} . At the highest doping level (2%), the reduced degradation efficiency was ascribed to the formation of Bi^{3+} clusters, rather than a homogeneous distribution and lower crystallinity. Anandan et al.2007 compared the photocatalytic activity of la-doped ZnO with pure ZnO and TiO_2 for the degradation of monocrotophos (MCP) Of the catalysts investigated, the efficiency of 0.8wt% La-doped ZnO was 2.5 and 1.5 times higher compared to pure ZnO and TiO_2 catalyst for the degradation of MCP both at wave lengths 254 and 365 nm respectively. In addition to high roughness and porous surface, this effect was attributed to a strong absorption of OH- ions on the surface of ZnO due to a large number of oxygen vacancies. Devi et al.2009a examined the effects of V^{5+} , Mo^{6+} and Th^{4+} doping into TiO_2 matrix for the degradation of chlorpyrifos under UV/solar irradiation. Undoped TiO_2 showed the highest rate constant ($3.1 \times 10^{-2} \text{ min}^{-1}$) compared to all the doped

TiO₂ samples under UV light. This may be due to the fact that mid band gaps created by the dopants may serve as site for recombination. The optimum dopant concentration of all catalysts was found to be 0.06%. Of all the catalysts, 0.06% Th⁴⁺doped-TiO₂ showed enhanced photocatalytic activity compared to all other catalysts under solar light due to (i) the large surface area, (ii) large shift in the bandgap,(iii) higher concentration of surface adsorbed water and hydroxyl groups (iv) effective separation of electrons and holes. The larger shift in the absorption band (460 and 482nm) to visible region increases the efficiency of the photocatalysts to absorb more photons under solar light. [Devi et al.2009b](#) tested the efficacy of TiO₂ doped with Th⁴⁺,V⁵⁺, and Mo⁶⁺ for the photocatalytic degradation of imidachloprid under solar light. The dopant amount of each metal ion was ranged from 0.02% to 0.1%. Th⁴⁺(0.06%)-TiO₂ showed enhanced activity and its efficiency was 2.8 times higher compared to P-25 under solar light compared to all the other catalysts studied. Due to the presence of Th⁴⁺, the band gap of TiO₂ was reported to lower 2.5 and 2.6 facilitating solar light absorption. Detrapping of the trapped charge carriers depends on electronic configuration and the oxidation state of the dopants. [Fresno et al.2005](#) compared the photocatalytic activity of Sn-doped TiO₂ with P-25 TiO₂ for the degradation of chlorsulfuron. Sn-doped TiO₂ was reported to show higher photocatalytic activity in comparison to undoped TiO₂ due to incorporation of Sn⁴⁺ into the TiO₂ lattice.

Table 6 The influence of dopant concentration on photocatalytic activity of photocatalyst

Pollutant	Light source	Photocatalyst	Doping	Optimum doping	Ref.
			(%)	(%)	
Diuron	UV	Pt-TiO ₂	0-2.0	0.2	Katsumata et al.2009
Monocrotophos	Solar	La-ZnO	0-1.0	0.8	Anandan et al.2007
2,4-DCAA	Visible	CeO ₂ -TiO ₂	0-10.0	5.0	Galindo et al.2008
Methylparathion	UV	Bi ³⁺ -TiO ₂	0-2.0	1.5	Rengaraj et al.2005
4-chlorophenol	Visible	N-TiO ₂	0.21-0.45	0.45	Sun et al.2009
Clopyralid	Visible	Fe ³⁺ -TiO ₂	0.13-1.48	1.27	Šojić et al.2010
Mecoprop, MCPP	Visible	Fe ³⁺ -TiO ₂	0.13-1.48	0.13	Šojić et al.2010
o-cresol	Visible	Pt-TiO ₂	0-1.0	0.5	Chen et al.2007
Lindane	Visible	Ag-TiO ₂	0-2.5	1.5	Senthilnathan and Philip 2010
Lindane	Visible	Cr-TiO ₂	0-2.5	2.0	Senthilnathan and Philip 2010
Beta-cypermethrin	UV	RuO ₂ -TiO ₂	0.1-0.8	0.3	Yao et al.2007
Methamidophos	UV	Re-TiO ₂	2.0-6.0	5.0	Zhang et al.2009
Oryzalin	Solar	Th-TiO ₂	0-0.1	0.06	Devi and Murthy 2009a
Acetamiprid	UV	Ag-TiO ₂	0-0.12	0.75	Cao et al.2008
Chlorsulfuron	UV	Sn-TiO ₂	0-0.2	0.11	Freshno et al.2005
Phenol	UV	Ag-ZnO	0-1.0	0.75	Liqiang et al.2006
Phenol	UV	Pd-ZnO	0-1.0	0.5	Liqiang et al.2006

Devi and Murthy 2008 investigated the effectiveness of Mo⁶⁺ doped-TiO₂ for the photocatalytic degradation of tebuconazole under UV and visible light. In the presence of UV light, undoped catalyst showed higher activity than doped catalyst. However, 0.06% Mo⁶⁺doped-TiO₂ showed enhanced photocatalytic activity under visible light irradiation. In the presence of TiO₂-Ag, Yan et al.2005 indicated that the degradation rates of dimethomorp were 71.5% compared to 45.5% with pure TiO₂ in under 5 days sunlight. Cao et al.2008 examined the efficacy of Ag-doped TiO₂ for the photocatalytic degradation of acetamiprid for a range of Ag content (0-0.12). At low level doping (0.02-0.06), anatase grain sizes decreased and the specific surface areas of TiO₂ increased. Ag dopant was found to accelerate the transformation of TiO₂ from anatase to rutile phase. At high level doping (0.08-0.12), particle size aggregation was reported to increase. The photocatalytic degradation rate constant was reported to increase rapidly when the Ag content ranged from 0.02 to 0.06 and then decreased slowly as the Ag content increased from 0.06 to 0.12. Shifu and Gengyu 2005 studied the SiO₂ content on the photocatalytic activity of TiO₂.SiO₂ beads for degradation of MCP. The optimum content of SiO₂ was reported to be 0.2. Devi and Krishnamurthy 2009 compared the photocatalytic degradation efficiency of diclofop-methyl using TiO₂ and BaTiO₃ under UV light irradiation. BaTiO₃ is shown to be more efficient than TiO₂ in the presence of ammonium persulfate. Rengaraj and Li 2006 tested the photocatalytic activity of Ag-TiO₂ prepared by ultrasonic assisted sol-gel method for the photocatalytic degradation of BPA. The presence of Ag in TiO₂ is reported to improve the degradation of BPA. Compared to pure TiO₂, the efficient electron-hole separation in Ag-TiO₂ was observed to increase the BPA degradation. Liqiang et al.2006 investigated the effect of Ag and Pd doping (0-1.0wt %) on the photocatalytic degradation of phenol using ZnO nanoparticles. The Ag and Pd modified ZnO was shown to have enhanced activity compared with pure ZnO because the modified ZnO can promote the adsorbed O₂ capturing photoinduced electrons to produce •O₂. Under the studied conditions, the optimum amount of doping was observed to be 0.75wt.% and 0.5 wt % for Ag and Pd respectively. The surface hydroxyl content of 0.5% Pd-ZnO is reported to be larger than that of 0.5% Ag-ZnO, which is responsible for the higher activity than 0.5% Ag- ZnO. At pH 9, Chen et al.2007 tested the effect of Pt dosage (0.04-1.5wt %) on the photocatalytic activity of TiO₂ for the decomposition of 9mg/L o-cresols under visible light. The band gap energies were observed to be 3.11eV for pure TiO₂ and 2.95eV for 1.5 wt% Pt/TiO₂. More than 90% o-cresols were shown to be decomposed by 0.50wt % Pt-TiO₂.The degradation rate constants of o-cresol for the 0.50wt% Pt-TiO₂ was 4.8 times than that obtained with pure TiO₂. The presence of Ti³⁺ prevents the recombination of e⁻/h⁺ due to the formation of Schottky Barrier between platinum and TiO₂. Amadelli et al.2008 investigated the influence of cobalt (Co) addition (0.05-0.5%) on the performance of TiO₂ for the degradation of 1mM 4-CP with visible light ($\lambda>450$ nm). Under the conditions tested, 0.2% Co-doped TiO₂ is shown to be efficient. After 30 min irradiation, 0.5%Co-TiO₂ calcined at 400°C showed superior activity compared to undoped TiO₂ for the degradation of BPA and 4-CP in visible light ($\lambda>420$ nm; $\lambda>450$ nm) irradiation. Lin et al.2006 investigated the activity of four metals (Ag, Au, Pt, and Cu) doped TiO₂ for the photocatalytic degradation of pentachlorophenol (PCP). All four metals doped TiO₂ samples showed strong visible light (400-800 nm) absorption and enhanced activity due to reduced e⁻/h⁺ recombination and smaller particle size which

increases surface areas. The surface areas of TiO_2 , Ag-TiO_2 and Au-TiO_2 are reported to be 78.3, 84.6, and 86.0 m^2/g , respectively. The effect of metal contents on the photocatalytic efficiency was observed to follow the trend $0.1 > 0.5 > 1.0 \text{ wt\%}$. The quantum yields of PCP degradation ranged from 9.9×10^{-3} to 13.6×10^{-3} . [Iliev et al.2010](#) studied the photocatalytic activity of TiO_2 , Au/TiO_2 , N-doped TiO_2 and Au/N-TiO_2 synthesized by sol-gel method for the degradation of oxalic acid under UV, visible and combined UV-visible light irradiation. The average size of the TiO_2 and N-doped TiO_2 is 20 nm and the average size of Au/TiO_2 and Au/N-TiO_2 is ≈ 5 nm. In the UV light, the rate constants of oxalic acid by the studied samples follow the order $\text{Au/N-TiO}_2 > \text{Au/TiO}_2 > \text{N-TiO}_2 > \text{TiO}_2$. In the visible light, the rate constants of oxalic acid by the studied samples follow the order $\text{Au/N-TiO}_2 > \text{N-TiO}_2 >> \text{Au/TiO}_2 > \text{TiO}_2$. The rate constants using Au/N-TiO_2 are shown to be 0.085 and 0.012 $\text{mmol L}^{-1} \text{ min}^{-1}$ in UV and visible light respectively. Using N-TiO_2 and Au/N-TiO_2 , nearly similar degradation rate constants are noticed in UV and UV-visible light. They reported that the absorption edge of TiO_2 was shifted from 340 nm in UV to 450nm in visible region. [Venkatachalam et al.2007b](#) tested the effect of Zr^{4+} doping(0.5-5.0 mol % Zr^{4+}) in TiO_2 matrix for the photocatalytic degradation of 4-CP using sol-gel method. The photocatalytic activity of 3.0 mol% Zr^{4+} -doped TiO_2 was shown to be superior compared to nano TiO_2 and P-25 due to enhanced adsorption of 4-CP over the catalyst surface and the smaller particle size.

[Kim et al.2005](#) tested the efficacy of TiO_2 doped with 1.0 wt% transitions metals such as Fe, Cu, Nd, Pd and Pt for the dgerdation of 4-CP. After 240 min irradiation, the extents of degradation are shown to be about 90%, 75% and 65% for Pt-TiO_2 , Pd-TiO_2 and pure TiO_2 respectively. This is related to the suppression of electron/hole recombination due to trapping of electrons. However, the Fe and Cu (1.0 wt%)-doped TiO_2 shows lower degradation efficiencies compared to pure TiO_2 . The reduction of Cu^{2+} by photo-generated electrons may compete with the formation of superoxide anion-radicals and consequently may reduce the formation of peroxidic species, destroying phenol molecules. They also studied the effect of Pt and Pd contents (0-3.0 wt%) on the photocatalytic degrdataion of 4-CP and the optimum doping level was reported to be 2 wt% under the conditions examined. [Zaleska et al.2008](#) tested the photocatalytic activity of TiO_2 modified with boric acid for the degradation of phenol under UV and visible light, respectively. The use of boric acid as a boron source resulted in lower photocativity of obtained B- TiO_2 than pure TiO_2 under UV light. All the tested TiO_2 powders with boric acid series have almost the same photactivity under visible light. [Naeem and Ouyang 2009](#) studied the effect of Fe^{3+} doping (0-3.0 mol% Fe^{3+}) on the photocatalytic activity of TiO_2 for the degradation of phenol under UV light. Fe^{3+} -doped TiO_2 was reported to possess the anatase structure with a range of crystal size 8-11nm. The highest degradation efficiency was found at 0.5mol% Fe^{3+} -doped TiO_2 . In visible light irradiation, about 60% methyl orange ($\text{Co}=150\text{mg/L}$) was degraded in 4h with SO_4^{2-} -modified TiO_2 compared to only 33% with pure TiO_2 ,which was due to increased BET surface area, smaller crystallite size and increased number of reaction sites ([Parida et al.2008](#)). Following 2h calcination at 600°C , photocatalytic activity of La-doped TiO_2 was ranked in the order $1 > 1.5 > 3 > 0.5 > 5 > 0 \text{ mol\%La}$ for phenol degradation ([Liqiang et al.2004](#)).

[Venkatachalam et al.2007c](#) compared the photocatalytic activity of 0.5-3.0 mol% Mg^{2+} and 1-3.0mol % Ba^{2+} -doped TiO_2 synthesised by sol-gel technique for the degradation of BPA. The band gap values of Mg^{2+} and Ba^{2+} -doped TiO_2 were reported to be higher compared to pure TiO_2 . The degradation of BPA was found to be higher for metal doped TiO_2 than both pure nano TiO_2 and P-25. This was related to the enhanced adsorption of BPA over the catalyst surface and the decrease in particle size due to Mg^{2+} and Ba^{2+} loadings. The pure TiO_2 nanoparticles gave both anatase and rutile phases together, but the metal ion in TiO_2 gave only anatase phase. [Fan et al.2009](#) compared the efficacy of N-Fe co-doped TiO_2 prepared by sol-gel method for the degradation of methylene blue (MB) with TiO_2 under solar light. After 90 min irradiation, the degradation was observed to be about 80% with N-Fe co-doped TiO_2 compared to 45 % with pure TiO_2 . This was attributed to the shifting of the absorption edge in co-doped sample. Under visible light (>380nm) irradiation, [Zhu et al.2006](#) tested the photocatalytic activity of Fe^{3+} -doped TiO_2 for the degradation of 2, 4-DCP. After 7h reactions, the average photonic efficiencies were reported to be 8.36×10^{-6} and 5.12×10^{-6} for 0.15 Fe^{3+} - TiO_2 and P-25 respectively. This was related to small crystal size, high specific surface area, mesoporous structure, surface chemisorbed water and hydroxyl groups. In visible light irradiation, [Silva et al.2009](#) noted an optimum Ce content of 0.6 %(w/w) in TiO_2 matrix in the enhanced degradation of 4-CP. In addition to the retardation of phase transformation, this behaviour was related to the shift of the TiO_2 absorption edge towards longer wavelengths, by reducing the band gap of original material. [Kim et al.2008](#) studied the photocatalytic degradation of 4-CP using anatase, rutile, Ni 8-wt%-doped TiO_2 powders (anatase and rutile) under UV and visible light irradiation. Under UV and visible light irradiation, the effectiveness of Ni 8 wt%-doped TiO_2 ($234\text{ m}^2/\text{g}$) was much higher than that of other powders ($100\text{-}150\text{ m}^2/\text{g}$). [Adan et al.2007](#) investigated the effect of Fe^{3+} doping (0.4-5.1 wt %) on the photocatalytic degradation of phenol. The photocatalytic activity was shown to be enhanced following doping with Fe^{3+} up to ca.1wt%. Doping above ca.3wt% did not result in any enhancement of the catalytic activity. [Jin and Shiraishi 2004](#) tested the photocatalytic activity of Pd, Cu and Pt deposited TiO_2 either individually or simultaneously for the degradation of 2,4-DNP(Co=8mg/L). After 180 min, nearly complete degradation was achieved with the metals doped TiO_2 whereas only 81.25% degradation obtained with bare TiO_2 . The pattern of degradation was ranked in the order: $Pd/TiO_2 > Pd-Cu/TiO_2 > Pd-Cu-Pt/TiO_2 > Cu/TiO_2 > TiO_2$. [Wang et al.2007](#) studied the synergistic effects of Cu^{2+} and F^- ions on the photocatalytic degradation of phenol. The degradation rate constant (k) was shown to be 0.010 min^{-1} in the absence of Cu^{2+} and F^- . The addition of 0.4 mmol L^{-1} Cu^{2+} increases k by 40% and the addition of 5 mmol L^{-1} F^- improves k by ca. 120%, and the co-addition of 0.4 mmol L^{-1} Cu^{2+} and 5 mmol L^{-1} F^- enhances k further by ca. 310%. The observed synergistic effect of Cu^{2+} and F^- ions was attributed to the surface modification of photocatalyst by adsorbed Cu^{2+} and F^- ions.

3.11.2 Influence of non-metals doping

The metal doping can result in thermal instability of doped TiO_2 , electron trapping by metal centres, and requirement of expensive ion-implantation facilities. Recent investigations indicate that the desired band gap narrowing of TiO_2 can be better achieved by employing non-metal elements such as N, F, S and C.

Such modified TiO₂ showed stronger absorption in the visible region owing to band gap narrowing and enhanced the degradation of organic pollutants under visible light irradiation, especially under solar light. The photocatalytic activity of anatase crystal phase N-doped TiO₂ for the degradation of mecoprop and (4-chloro-2-methylphenoxy) acetic acid (Co=2.7mmol/dm⁻³) under visible light (400-800nm) irradiation was reported to be 1.5 times higher compared to P-25 ([Abramovic et al.2009](#)). Carbon doped TiO₂ was reported to be efficient for the degradation of phenol (Co=30 mg/L) under visible light ($\lambda>420\text{nm}$) irradiation due to the shifting of absorption edge to a lower energy level ([Lee et al.2008](#)). [Anandan et al.2009](#) compared the performance of IO₃⁻ doped TiO₂ with pure TiO₂ for the degradation of MCP (Co=40mg/L) at wavelengths 254 and 365nm. The degradation rate constant of IO₃⁻doped TiO₂ (1 wt%) was shown to be nearly three times higher than pure TiO₂. However, the rate constant and relative photonic efficiencies for the degradation of MCP were smaller at 365nm compared to 254nm due to enhanced electron-hole recombination at wavelength 365nm. The enhanced photocatalytic activity of IO₃⁻ doped TiO₂ was related to the IO₃⁻doping which serves as an electron trap during the photocatalytic reaction, eventually suppressing the recombination of electron-hole pairs. In addition, the high activity of IO₃⁻doped TiO₂ was strongly dependent on the particle size, shape, surface area, formation of mixed phases, and distribution of iodine particles on titanium surfaces. At wavelengths 254 and 365nm, the relative photonic efficiencies of 1wt% IO₃⁻ doped TiO₂ systems were shown to be 2.5 and 2.0 times greater than pure TiO₂. Under UV (365nm) and visible light(> 400nm) irradiation, [Senthilnathan and Philip 2010](#) studied the photocatalytic degradation of N-doped TiO₂ prepared by sol-gel method using triethylamine, urea, ethylamine and ammonium hydroxide for the degradation of 3.44×10^{-4} mmol lindane. The band gap energies of all N-doped TiO₂ samples (1:0.8, 1:1.2, 1:1.6 and 1:2.0 ratio) were lower compared to P-25 and anatase TiO₂ and the absorption of light in the range 400 to 600nm was stronger after nitrogen doping. In addition, the absorption increases with increasing doping concentration from 1:0.8 to 1:2.0. In comparison to urea, ammonium hydroxide and ethylamine, triethylamine doped TiO₂ showed greater photocatalytic activity since it forms a stable organo titanium complex which plays a very important role on the stability of the nano-particles and avoids the growth and aggregation of the particles ([Yu et al.2007](#)). Using P-25 and anatase TiO₂, degradation of 5.17×10^{-4} mmol lindane was shown to be 100% under UV light, whereas only 13.24% and 20.68% degradation was reported in visible light. However in the presence of N-doped TiO₂, 37.5% and 100% of degradation of lindane was observed under UV and visible light, respectively. Under visible light ($\lambda\geq 400\text{ nm}$), [Cheng et al.2007](#) tested the photocatalytic activity of carbon-modified TiO₂ for the degradation of 0.15mM 4-CP. C-doped TiO₂ is shown to have large surface area. The first order rate constant for the C-TiO₂ and P-25 are observed to be 6.1×10^{-3} and $1.0\times10^{-3}\text{ min}^{-1}$, respectively. [Huang et al.2006](#) reported that N-F co-doped TiO₂ showed higher photocatalytic activity for p-chlorophenol under visible light irradiation (400-500nm). Under the conditions examined, the degradation efficiency was shown to be 1.75, 1.25 and 1.5 times higher compared to P-25, N-doped TiO₂ and F-doped TiO₂ respectively. This behaviour was ascribed to a synergistic effect of surface acidity, and doped N and F atoms. [Xing et al.2009](#) showed that N-doped TiO₂ synthesized by ammonium nitrate and ammonia as a nitrogen sources showed maximum photocatalytic activity for the degradation of 2,4-DCP (Co=100mg/L)

within 5h of irradiation under visible light. Similar study using N-doped TiO₂ was reported by Cong et al.2007 with 2,4-DCP (Co=100mg/L) and rhodamine B (Co=20mg/L) under visible light and complete degradation was achieved within 5h and 1h irradiation respectively. Huan et al. 2007 tested the decomposition of 4-CP (Co=13mg/L) using N-doped TiO₂ under visible light and achieved 63.5% degradation within 6h irradiation. Kun et al.2009 examined the photocatalytic activity of phenol (Co=0.5mmol/L) under visible light with N-doped TiO₂ and found that acid treated N-TiO₂ showed higher catalytic activity in 2h irradiation.Under visible light, Ananpattarachai et al.2009 investigated the photocatalytic efficacy of N-TiO₂ prepared with different nitrogen dopants for the degradation of 2-CP. The photocatalytic activity of all N-doped TiO₂ ranked in the following order: TiO₂/diethanolamine>TiO₂/triethylamine >TiO₂/urea > un-doped TiO₂. After 50 min irradiation, 2-CP removal was 66% for TiO₂ doped with diethanolamine whereas only 3% and 14% 2-CP removal was obtained with P-25 and undoped TiO₂ respectively. This increase is related to the strong absorption in the visible light region and a red-shift in the bandgap transition of the doped TiO₂ with nitrogen dopant.Under visible light ($\lambda \geq 420\text{nm}$) irradiation, Šojić et al.2010 studied the photocatalytic degradation of herbicides mecoprop (MCPP), 4-chloro-2-methylphenoxy acetic acid (MCPA) and cropyralid(CP) using Fe³⁺ or N-doped TiO₂. Rutile TiO₂ doped with Fe³⁺ showed lower photocatalytic activity for the degradation of MCPP and MCPA. In contrast, the rate of CP degradation is shown to increase with increase in the Fe³⁺ content up to 1.27 at.%. When N-doped anatase TiO₂ was used, the rate of degradation of all three herbicides was higher compared to that obtained using undoped anatase TiO₂. In all the cases the photocatalytic efficiency of undoped anatase TiO₂ was higher compared to that of the undoped rutile form. Herrera et al.2009 tested the photocatalytic activity of N,S co-doped and N-doped commercial anatase TiO₂ powders for the degradation of phenol under simulated solar irradiation. Undoped P-25 was shown to have the highest photocatalytic activity. N,S co-doped powders showed similar photocatalytic activity as undoped TKP 102(Tayca) while N-doped TKP 102 was less active photocatalyst due to N impurities on the TiO₂ acting recombination centres. Wang et al.2005 compared the photocatalytic degradation of phenol in the presence of N-doped TiO₂ and P-25 under visible and sunlight irradiation. The photocatalytic activity of the N-doped TiO₂ with anatase phase is shown to be higher than that of the P-25 under visible light irradiation. P-25 exhibits higher photoactivity for the degradation of phenol compared to N doped-TiO₂.

3.12 Evaluation of Energy Efficiency

In heterogeneous photocatalytic water purification process, the generation of photons driven by UV and solar light for catalyst activation is the significant part of the total cost for the operation of the system. The evaluation of the treatment costs is, at this time, one of the aspects that need more attention. In order to select a purification system for storm and wastewater reuse, a number of important factors; including economics, economy of scale, regulations, effluent quality goals, safe operation, and robustness should be taken into considerations. While all these factors are important, economics is often paramount. Simple figures-of-merit that provide a direct link to the electric-or solar-energy efficiency of an advanced

oxidation process (AOP), have been recommended for comparison by IUPAC. Several researchers (Wu et al.2009a, 2009b; Daneshvar et al.2006, 2007) evaluated the energy efficiency of the photocatlytic water purification system for degradation of various organic contaminants in water. Bolton et al.2001 defined the figures-of-merit “electrical energy per mass” (E_{EM}) for use in the zero-order kinetic regime and “electrical energy per order” (E_{EO}) for use in the first-order kinetic regime for low and high contaminant concentrataions respectively in AOPs. Daneshver et al.2007 evaluated the E_{EO} for the photocatalytic degradation of the insecticide diazinon. In the case of photocatalytic (particle size 14 nm) process, the E_{EO} value was reported to be 1075.3kWh/m³ compared to only 20,000kWh/m³ in photolysis system. Wu et al.2009a indicated that the photocatalytic degradation of pesticide turbufos could be efficiently achieved with an E_{EO} value of 71kWh/m³. Wu et al.2009b reported that phorate could be treated easily and effectively using UV/TiO₂ system with an E_{EO} value of 96kWh/m³ order. Using P25 and rutile TiO₂, the E_{EO} values for the photocatalytic degradation of eriglaucine are reported to be 175.44 and 10,000.00 kWh/m³ respectively (Daneshvar et al.2006). Bandala et al.2007 compared the four different solar collectors based on figures-of-merit for the photocatalytic degradation of oxalic acid and carbaryl when the incident solar radiation was 1000W/m². Under the conditions tested, compound parabolic collector (CPC) and V trough collector (VTC) systems were demonstrated to be efficient for the degradation of both pollutants. The flat tubular (FT) collector has been reported to be inefficient probably due to its poor radiative flux distribution. The capital cost of a solar collector is proportional to its area and hence figures-of-merit based on the solar collector area are considered appropriate. The E_{EO} determination is essential, however, the costs associated with chemicals and capital outlays should also be considered to gain an overall picture of the process economics.

4. CONCLUSION

This review focuses on the recent advancements in heterogeneous photocatalysis system related to purification of water and wastewater. The role of various operating parameters on the photocatalytic degradation of various pesticides and phenols has been explored in this article. TiO₂ has been suggested to be an efficient and viable photocatalyst for the degradation and mineralization of various toxic organic pollutants such as pesticides and phenolic compounds in water in the presence of UV, visible or solar light and oxygen. The reported results also suggest that various operating parameters such as photocatalyst type, light intensity, pollutant types and initial concentration, catalyst amount, initial pH of the reaction medium, catalyst application mode, oxidizing agents/electron acceptors, and the presence of ionic components in solution can significantly influence the photocatalytic degradation rate of pesticides and phenols. Optimizing the degradation parameters is crucial from the perspective of efficient design and the application of photocatalytic oxidation process to ensure sustainable operation. The application of this technique for realworld wastewaters calls for further investigation to achieve stable pollutant removal through the optimization of process parameters. This would make a significant impact on the potential commercial application of this technique to industrial system. Metal and non-metal doped TiO₂ have been reported to result in improved degradation rate. Although the advances in TiO₂ photocatalysis using doped

materials have been tested for relatively simple and clean solution, the sustainability of their photocatalytic activity in real wastewater is unclear which essentially requires further attention. On the technical front, the advances summarized in this article must be translated into large-scale systems capable of continuously and reliably treating large volumes of real wastewaters. In spite of extensive investigations, the commercial exploitation of photocatalysis has been hindered by the lack of efficient and low-cost visible light harvesting catalyst, a relatively poor understanding of the photoreactor design, and inadequate scale up strategies. The development of a more reliable and low-cost photocatalyst that can be activated by visible and solar light or both should be explored for potential application in wastewater treatment. In addition, more work is required on the modeling of photoreactor to optimize its design for the pollutant degradation. In the literature, there is currently limited information on the modeling of photoreactor to optimize its performance. Recent research has demonstrated the applicability of computational fluid dynamics (CFD) to the modelling of photocatalytic reactors. It shows promise in its flexibility to vary parameters for optimisation of reactor design. Present research activities at CQ University and QUT, Australia focus on the computational fluid dynamics modeling of a flat plate reactor to optimize its design and to predict its performance. Although this review is not comprehensive on the photocatalytic degradation of organic pollutants, however, it does address the fundamental principles and recent applications in this area.

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