Heterogeneous Photocatalytic Degradation of Phenols in Wastewater: A Review on Current Status and Developments

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ABSTRACT

In recent years, there has been an enormous amount of research and development in the area of heterogeneous photocatalytic water purification process due to its effectiveness in degrading and mineralising the recalcitrant organic compounds as well as the possibility of utilising the solar UV and visible spectrum. One hundred and twenty recently published papers are reviewed and summarised here with the focus being on the photocatalytic oxidation of phenols and their derivatives, predominant in waste water effluent. In this review, the effects of various operating parameters on the photocatalytic degradation of phenols and substituted phenols are presented. Recent findings suggested that different parameters, such as type of photocatalyst and composition, light intensity, initial substrate concentration, amount of catalyst, pH of the reaction medium, ionic components in water, solvent types, oxidising agents/electron acceptors, mode of catalyst application, and calcination temperatures can play an important role on the photocatalytic degradation of phenolic compounds in wastewater. Extensive research has focused on the enhancement of photocatalysis by modification of TiO_2 employing metal, non-metal and ion doping. Recent developments in TiO_2 photocatalysis for the degradation of various phenols and substituted phenols are also reviewed.

Key Words: Phenols, Substituted phenols, Photocatalysis, Water purification

1. Introduction

Recycling of wastewater effluent is recognised to be a strategic approach in a sustainable water management portfolio by water utilities both in Australia and in other parts of the world to minimise the growing water demand in a water-scarce environment [1-3]. The widespread occurrence of phenols in waste water and associated environmental hazards has heightened concern over public health [4]. Phenols and their derivatives are well known for their bio-recalcitrant and acute toxicity. Phenols are being introduced continuously into the aquatic environment through various anthropogenic inputs. The presence of toxic organic compounds in storm and waste water effluent is reported to be a major impediment to the widespread acceptance of water recycling [5,6]. Further, their variety, toxicity and persistence can directly impact the health of ecosystems and present a threat to humans through contamination of drinking water supplies e.g., surface and ground water [3,4]. In response it has become a challenge to achieve the effective removal of persistent organic pollutants from waste water effluent to minimise the risk of pollution problems from such toxic chemicals and 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, rivers and lakes at low concentration. Despite their low concentration, these contaminants are a major health concern because of their extremely high endocrine disrupting potency and genotoxicity [7]. These findings enunciate the necessity for further research on the removal of trace contaminants to minimise their accumulation, particularly prior to indirect or direct reuse of reclaimed water. Conventional wastewater purification systems such as activated carbon adsorption, membrane filtration, chemical coagulation, ion exchange on synthetic adsorbent resins, etc., also generate wastes during the treatment of contaminated water, which requires additional steps and cost. In recent years, the heterogeneous photocatalytic oxidation (HPO) process employing TiO_2 and UV light has emerged as a promising new route for the degradation of persistent organic pollutants, and produces more biologically degradable and less toxic substances [8,9]. This process is largely 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 ones into relatively innocuous end products such as CO_2 and H_2O. In the HPO process, destruction of recalcitrant organics is governed by the combined actions of a semiconductor photocatalyst, an energetic radiation source and an oxidizing agent. Moreover, the process can be driven by solar UV or visible light. Near the earth's surface, the sun produces 0.2-0.3 mol photons $m^{-2}h^{-1}$ in the range of 300-400nm with a typical UV flux of 20-30 Wm^2 .This suggests using sunlight as an economically and ecologically sensible light source [10]. As a result, development of an efficient photocatalytic water purification process for large scale applications has received considerable attention.

Although heterogeneous photocatalysis appears in numerous forms, the photocatalytic degradation of phenol and substituted phenols in wastewater has recently been the most widely investigated. Several reviews [11,12] focusing briefly on the available technologies for the abatement of phenolic compounds in wastewater have recently been published. In light of the basic and applied research reviewed, the photocatalytic oxidation method appears to be a promising route for the treatment of wastewater contaminated with phenol and phenolic compounds. However, the major drawbacks still encountered are low quantum efficiency due to inefficient visible light harvesting [13], the design of the photoreactor [14], the recovery and reuse of titanium dioxide [15], the generation of toxic intermediates [16,17], and concern about catalyst deactivation [18]. Information from various investigations suggests that the photocatalytic degradation of phenol and its derivatives is mainly dependent on the solution pH, catalysts and their composition, organic substrate type and concentration, light intensity, catalyst loading, ionic composition of waste water, types of solvent, oxidant concentration, and calcination temperatures. Understanding the impacts of various parameters on the photocatalytic degradation efficiency is of paramount importance from the design and operational points of view when choosing a sustainable, efficient technique for the treatment of waste water. This paper aims to review and summarise the role of important operating parameters on the photocatalytic degradation of phenols in wastewater together with recent achievements. Recent research on the modified TiO_2 photocatalysis under visible and/or solar light aimed at improving

phenols degradation in wastewater by means of metal, non-metal and ion doping is also highlighted in this review. The existing limitation and future research needs associated with the treatment technology pertaining to the contaminant of interest are also discussed.

2. Photocatalytic Oxidation Process

2.1 Principle of Photocatalysis

In the photocatalytic oxidation process, organic pollutants are destroyed in the presence of semiconductor photocatalysts (e.g., TiO_2, ZnO), an energetic light source, and an oxidising agent such as oxygen or air. Fig.1 illustrates the mechanism of TiO_2 photocatalysis. 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. 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_v^+) in the valence band and an electron (e^-) in the conduction band (CB). The positive hole oxidizes either pollutant directly or water to produce $\cdot OH$ radicals, whereas the electron in the conduction band reduces the oxygen adsorbed on the catalyst (TiO_2).
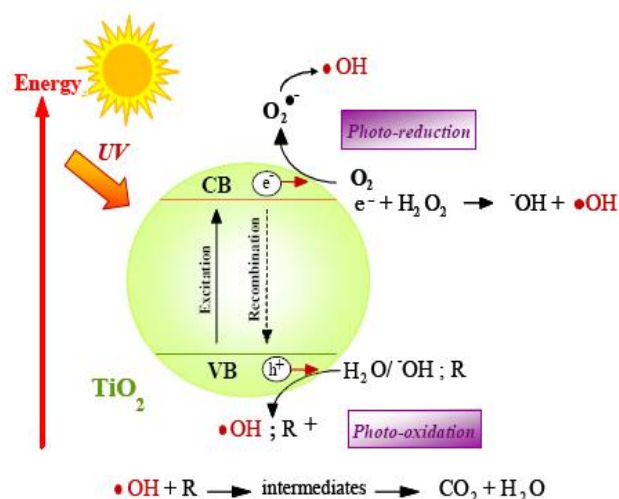
Fig.1 Schematic diagram illustrating the principle of TiO_2 photocatalysis

The activation of TiO_2 by UV light can be represented by the following steps:

$$TiO_2 + h_v \; \dashrightarrow \; e^- + h^+ \qquad (2.1)$$
$$e^- + O_2 \; \dashrightarrow \; O_2^{\cdot -} \qquad (2.2)$$
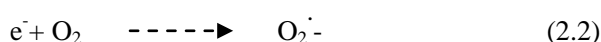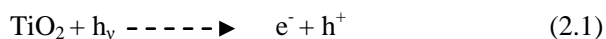
In this reaction, h^+ and e^- are powerful oxidizing and reductive agents respectively. The oxidative and reductive reaction steps are expressed as:

Oxidative reaction:

$$h^+ + Organic \; \dashrightarrow \; CO_2 \qquad (2.3)$$
$$h^+ + H_2O \; \dashrightarrow \; \cdot OH + H^+ \qquad (2.4)$$

Reductive reaction:

$$\cdot OH + Organic \dashrightarrow CO_2 \qquad (2.5)$$
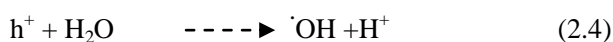
Hydroxyl radical generation by the photocatalytic oxidation process is shown in the above steps. In the degradation of organic pollutants, the hydroxyl radical, which is generated from the oxidation of adsorbed water where it is adsorbed as OH^-, is the primary oxidant; and the presence of oxygen prevents the recombination of an electron-hole pair. 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^+. Thus it is of paramount importance to prevent electron accumulation in efficient photocatalytic oxidation. In photocatalysis, TiO_2 has been studied extensively because of its high activity, desirable physical and chemical properties, low cost, and availability. Of three common TiO_2 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. Different light sources such as UV lamps and solar radiation have been used in previous investigations into the photocatalysis of various pesticide and herbicide derivatives dominant in storm water and wastewater effluent.

2.2 Phenol, Chlorophenol and Nitrophenol in Photocatalytic Medium

Phenol along with its chlorophenol and nitrophenol derivatives is highly soluble in water. The solubility of phenol, o-chlorophenol, m-chlorophenol, p-chlorophenol, o-nitrophenol, m-nitrophenol and p-nitrophenol is shown in Table 1. The main reaction site for their destruction during photocatalysis is the bulk liquid, where the attack of hydroxyl radicals on the ring carbons results in various oxidation intermediates. Hydroquinone, catechol, and p-benzoquinone are reported to be the major intermediates formed during the photocatalytic degradation of phenol [19]. Reaction intermediates such as chloro-hydroquinone, 4-chlorocatechol and resorcinol are eventually converted to acetylene, maleic acid, carbon monoxide and carbon dioxide [20].

Table 1 Solubility of phenol and its chloro and nitro-derivatives in water

Compound	Solubility (g/100g)	Ref.
Phenol	9.48	[21]
o-chlorophenol	2.04	[22]
m-chlorophenol	2.25	[22]
p-chlorophenol	2.77	[22]
o-nitrophenol	0.21	[23]
m-nitrophenol	2.19	[23]
p-nitrophenol	1.34	[23]

Chlorophenols are water pollutants of moderately toxicity and are suspected of carcinogenic properties. They originate from the natural degradation of chlorinated herbicides, the chlorination of phenolic substances and disinfection of water. Nitrophenols are water pollutants of high toxicity and they are released into the water environment due to the synthesis and use of organo-phosphorous pesticides, azo dyes, and some medical goods. The main byproducts detected during their photocatalytic degradation are 4-nitrocatechol, benzoquinone, hydroquinone and a number of organic acids. Fig.2 illustrates the photocatalytic degradation of phenol and the formation of intermediates. The •OH radical attacks the phenyl ring of the phenol yielding catechol, resorcinol,1,2,3-benzenetriol and hydroquinone, then the phenyl rings in these compounds disintegrate to give malonic acid, then short-chain organic acids such as, maleic, oxalic, acetic, formic 3-hydroxy propyl carboxylic acid, 2-hydroxy propanal , 2-hydroxy-ethanoic acid glycol acid, finally CO_2 and H_2O. H• produced during the attack of bonds by •OH is reported to be an important active free radical in the degradation process. During the process, H^+ or H• is scavenged by oxygen to form HO_2• radicals, which eventually convert to •OH radicals. Therefore, the principal reaction leading to organics decomposition would be the one with •OH radicals.
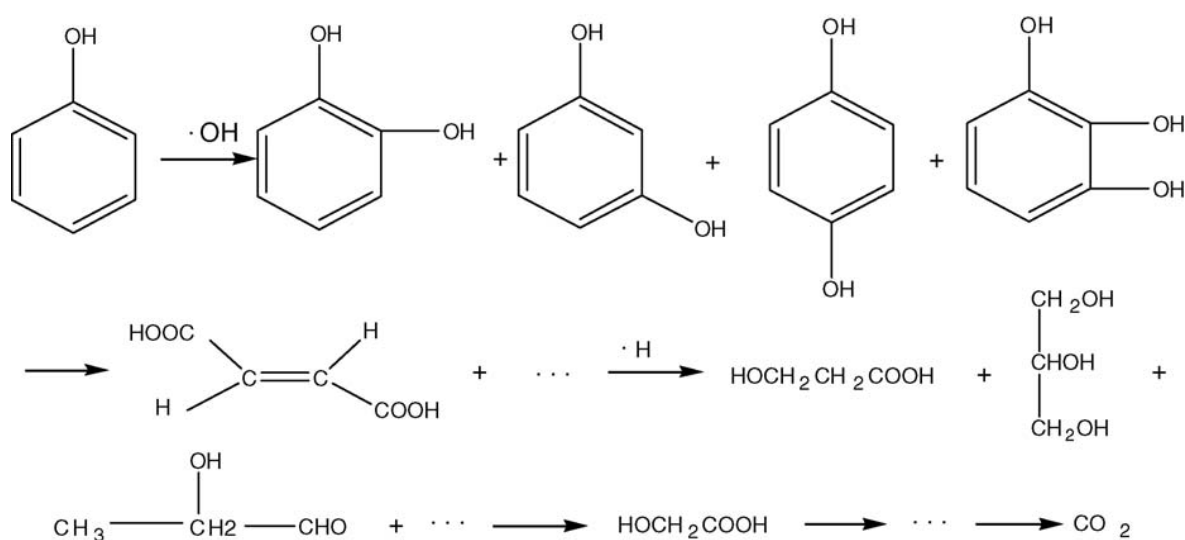
Fig.2 Photocatalytic degradation of phenol by nanomaterial TiO_2 in wastewater [24].

3. Influence of parameters on the photocatalytic degradation of phenols

3.1 Comparison of Catalyst and Substituted Group

The photocatalytic activity of TiO_2 is dependent on surface and structural properties of the 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 investigated for the photocatalytic degradation of phenolic compounds and dyes in aqueous environments. Table 2 shows the specification and characteristics of some

commercial TiO$_2$ 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 and TTP were also used for degradation of toxic organic compounds. P-25 contains 75% anatase and 25% rutile with a specific BET surface area of 50m^2/g and a primary particle size of 20nm [25]. Hombikat UV 100 consists of 100% pure and smaller anatase with a specific BET surface area of 250m^2/g and a primary particle size of 5nm [25]. The photocatalyst PC 500 has a BET surface area of 287m^2/g with 100% anatase and a primary particle size of 5-10nm [25], and TiO$_2$ obtained from TTP, India has a BET surface area of 9.82m^2/g. It has been demonstrated that the degradation rate of dyes proceeds much more rapidly in the presence of Degussa P-25 as compared to other photocatalysts. The efficiency of photocatalysts was shown to follow the order: P25>UV100>PC500>TTP for the degradation of various dyes [26-32]. The photocatalytic activity of Degussa P25 was reported to be higher due to slow recombination between electrons and holes whereas Hombikat UV 100 is reported to have a high photoreactivity due to fast interfacial electron transfer rate. The differences in the photocatalytic activity are related to the variations in the BET surface, impurities, existence of structural defects in the crystalline framework or density of hydroxyl groups on the catalyst surface.

Table 2

Specification and characteristics of commercial TiO$_2$ samples

TiO$_2$ sample	BET surface area (m^2/g)	Particle size (nm)	Composition
Degussa P-25	50	21	75% Anatase, 25% Rutile
Millennium PC 500	287	5-10	Anatase
Hombikat UV 100	250	5	Anatase
TTP	9.82	N/A	N/A

N/A=Not available

These factors could influence the adsorption behaviour of a pollutant or degradation intermediates and the life time and recombination rate of electron-hole pairs [27]. Some of the illustrative works in recent years is depicted in Table 3. Priya et al. [33] compared the photocatalytic degradation of nitrophenols using combustion synthesised nano-TiO$_2$ and Degussa P-25. The photodegradation kinetics was first order. The photocatalytic degradation rates were considerably higher in combustion synthesized TiO$_2$ compared to that of P-25. For both catalysts, the degradation rate was shown to follow the order 4-Nitrophenol> 2-Nitrophenol> 3-Nitrophenol> 2,4-Ditrophenol. The position of substitution is reported to affect the rate of degradation. Shukla et al. [34] compared the photocatalytic degradation efficiency of phenol, dichlorophenol (DP) and trichlorophenol (TCP) at 0.266mM solution concentration in the presence of UV-vis/ZnO/persulfate. Degradation of the tested compounds under simulated solar light alone was demonstrated to be negligible due to poor absorbance of light in the available wavelength. In comparison to phenol, chlorophenols degradation was significantly lower under the conditions examined. The order of

the degradation rate was found to be as phenol>DCP>TCP. The photocatalytic activity of ZnO was observed to be higher than TiO_2 for the degradation of phenolic contaminants under UV-vis light. Salah et al. [35] compared the efficiency of three commercial catalysts Degussa P25 (20nm), TiO_2-A1(160nm) and TiO_2-A2 (330nm) available in anatase form, and ZnO for the degradation of phenol. After 5h reactions, the order of the efficiency was shown to follow ZnO>P_{25}> TiO_2-A_1>TiO_2-A_2. The observed variation in the efficiency is related to the structure, diameter of particles and electrical properties of the photocatalyst. Peiro et al. [36] observed that the photocatalytic degradation of phenol and ortho-substituted phenolic compounds were shown to follow the order: Guaiacol>2-chlorophenol=Phenol> Catechol. Kusvuran et al. [37] 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

Table 3

Some representative work on the photocatalytic degradation of organic contaminants

Pollutant	Experimental conditions	Degradation rate	Ref.
Phenol	C_o phenol=50ppm, TiO_2=2g/l, under UV irradiation(λ_{max}=366nm)	92 % degradation achieved in 6h	[35]
Tri-substituted phenol; TCP, TBP, TMP	TiO_2=0.5g/l in 200ml, C_o=0.-0.5mM	100-56% TCP removal obtained in 1h. 70-44% TBP removal achieved in 1h. 60-22% TMP removal in 1h.	[37]
Phenol, DNP 4-NP, TNP	C_o=30mg/l, I=125W MP Hg, λ>290nm, TiO_2=0.5g/l,	Complete degradation of all nitro phenols occurs between 2 and 7h	[38]
Phenol DCP TCP	$C_{oPhenol}$=25ppm, C_{oDCP}= 44ppm C_{oTCP}=52ppm,ZnO=0.4g/l, Persulfate= 2g/l	85% degradation of TNP occurs in 150 min. 90% degradation of DNP occurs in 150min and 93% degradation of phenol occurs in 150 min.	[34]
Chrysoidine R[1] Acid Red 29[2]	C_o=0.22-0.25mM, 125W Mp Hg, TiO_2=1g/l, pH=4.3-5.2	92% degradation and 77% mineralisation of dye1 takes place after 1h irradiation. 98% degradation and 88% mineralisation of dye2 occurs in 2h	[26]
Amaranth[1] Bismarck[2]	C_o=0.4-0.5mM, 125W Mp Hg, TiO_2=1g/l, pH=3.25-5.68	Nearly complete degradation occurs in 75 min for dye1 and 40 min for dye 2	[26]
Acid blue 45[1] Xelenol orange[2]	C_o=0.3-0.4mM, 125W Mp Hg, TiO_2=1g/l, pH= not available	About 51 and 73% degradation of dye1 and dye2 takes place in 80 min irradiation time.	[30]
Bromothymol blue	C_o=0.25mM, TiO_2=1g/l, 125W Mp Hg, pH= not available	Nearly complete TOC removal achieved in 90 min.	[32]
Acridine Orange[1] Ethidium bromide[2]	C_o=1.0mM, TiO_2=1g/l, 125W Mp Hg, pH= not available	Complete degradation of dye1 and dye2 takes place in 75 and 195 min respectively.	[31]

was found to be in the following order: TCP> TBP> TMP and the degradation of di-substituted phenols was shown to be in the order: DCP>DBP> DMP. The degradation rate of the tested compounds was observed to be strongly dependent on the adsorption over catalyst, the electronic nature and number of the substituents and their position in the aromatic ring. Lacheb et al. [38] 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 degradation followed first order kinetics. The photocatalytic degradations of the tested compounds were shown to be in the following order: 2,4,6-TNP>2,4-DNP>4-NP>Phenol. However, for PC 500 supported on Ahlstrom paper 1048, the order is the opposite - Phenol>4-NP>2,4-DNP>2,4,6-TNP. The difference in poly nitrophenols disappearance rates was related to the variation in adsorption behaviour. For both supported Degussa P25 and Millennium PC-500 photocatalysts, the maximum quantities of adsorbed phenolic compounds increase in the order: Phenol<4-NP<DNP<TNP. Gulliard et al. [39] compared the photocatalytic efficiency of different catalysts with various surface areas, crystallite and particle sizes and their chemical of surface for the degradation of 4-chlorophenol. The observed order of efficiency based on the rate of degradation upon solar exposure was shown to be: TiONA PC 10 ($9m^2/g$)>P-25 ($50m^2/g$)>TiL COM HC 120 ($120m^2/g$)> Hombikat UV 100 ($250m^2/g$). The TiONA PC 10 photocatalyst has an activity about two times higher than Hombikat UV100 and TiL COM HC 120, and 1.4 times higher than that of P-25. All these catalysts have mainly the anatase structure. In the presence of P-25, Sevlam et al. [40] indicated that complete degradation of 4-flurophenol using P25 (BET = 55 m^2/g, particle size =30nm) was achieved in 60 min while complete degradation occurred in 90 min in the presence of ZnO (BET=$10m^2/g$, particle size=0.1-4μm). The higher efficiency of P-25 is due to its larger surface area compared to the ZnO. The oxidizing power of hydroxyl radicals produced by these catalysts is strong enough to break C-C, C-F and C=C bonds of 4-FP adsorbed on their surfaces leading to the formation of CO_2 and mineral acids.

Sobana et al. [41] compared the efficiencies of various catalysts (ZnO, TiO_2 anatase, ZnS, SnO_2, Fe_2O_3 and CdS for the degradation of Acid red 18 under UV irradiation. The highest degradation was achieved with ZnO over TiO_2 anatase catalyst due to the higher surface area of ZnO ($10m^2/g$) over TiO_2 anatase ($8.9m^2/g$). SnO_2, Fe_2O_3, CdS and ZnS have negligible activity on Acid Red 18 decolourisation due to their smaller band gaps which permit rapid recombination of hole and electron. Talebian et al. [42] compared the photocatalytic degradation efficiency of methylene blue (MB) under UV irradiation. The observed order of photocatalytic efficiency was shown to be SnO_2<ZnO<TiO_2<In_2O_3. The same trend was also observed at different pH values for the photocatalytic activities of different catalysts due to their various micro structures. Zhang et al. [43] compared the efficiency of coupled oxide ZnO-SnO_2 with ZnO or SnO_2 for the degradation of methylene orange (MO). The photocatalytic efficiency of ZnO-SnO_2 was significantly higher compared to ZnO or SnO_2 alone. Under the experimental conditions, the degradation of MO follows the first-order reactions during the first 15 min of irradiation, and the apparent rate constants for ZnO–SnO_2, Degussa P25 TiO_2, ZnO–SnO_2/NaOH, ZnO and SnO_2 are 0.0865, 0.0822, 0.0339,

0.0335, 0.0124 min^{-1}, respectively. The higher activity of ZnO-SnO$_2$ is attributed to its smaller size and the charge separation in coupled oxide. Cun et al. [44] compared the efficacy of ZS, pure ZnO and pure SnO$_2$ for the photocatalytic degradation of MO. The degradation efficiency was reported to follow the order of ZS>ZnO> SnO$_2$. The photocatalytic reaction by Z$_2$S is 40.2 and 66.1% faster than those by ZS and ZnO, respectively. The higher activity of ZS was related to the larger BET of ZS than ZnO, and the suppression of electron-hole pairs' recombination. Ksibi et al. [45] studied the photocatalytic degradation of six substituted phenols (2,4,6-TNP, Hydroquinone, 2,4-DNP, Resorcinol, phenol and 4-NP) over UV irradiated TiO$_2$. The adsorption constants were shown to decrease in the order: 2,4-DNP> Hydro> 4-NP> phenol> resorcinol>2,4,6-TNP. The higher value of 2,4-DNP (31 L/mol) was attributed to the ortho-position of nitro (-NO$_2$) group in the aromatic ring. In contrast the lowest adsorption constant of 2,4,6-TNP (1.45L/mol) is related to the big geometric hindrance due to the large number of nitro groups on the aromatic ring. The influence of the substituents on the photocatalytic degradation of phenols was reported to be Resorcinol>phenol.4-NP>2,4-DNP>Hydro>2,4,6-TNP. The variation in photoreactivity of these compounds is ascribed to the electronic character (electro-withdrawing or electro-donor) and to the position of the substituent groups in the aromatic ring.

3.2 Light intensity and wavelength

The light intensity determines the extent of light absorption by the semiconductor catalyst at a given wavelength. The rate of initiation for photocatalysis electron-hole formation in the photochemical reaction is strongly dependent on the light intensity [46]. Light intensity distribution within the reactor invariably determines the overall pollutant conversion and degradation efficiency [47]. Consequently the dependency of pollutant degradation rate on the light intensity has been studied in numerous investigations for various organic pollutants [48,49]. While in some cases the rate of reaction exhibited a square root dependency on the light intensity, others observed a linear relationship between the two variables [48-50]. Ollis et al. [49] reviewed the effect of light intensity on the organic pollutant degradation rate. It has been reported [48-50] that the rate is proportional to the radiant flux Φ for $\Phi < 25$mW/cm^2, and above 25mW/cm^2 the rate has been 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 was independent of light intensity. This is likely because, at low intensity, reactions involving electron-hole formation are predominant and electron-hole recombination is insignificant. Puma et al. [51] examined the effect of light wavelength on the photocatalytic degradation of 2-Chlorophenol (2-CP) using UV-A alone and individually with 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 initial rate of 2-CP degradation was found to be 1.8 times faster under UV-ABC radiation and the degradation of 2-CP was 98% in 20min. The enhanced degradation rate with UV-ABC was attributed to the photon flux with UV-ABC, which was reported to be 1.56 times higher 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. Kaneco et al. [52] investigated the effect of light intensity on the solar photocatalytic degradation of bisphenol A in water with TiO_2 on sunny and cloudy days. The degradation efficiency is shown to increase rapidly with increase in the light intensity up to $0.35mW/cm^2$, and then the efficiency increased gradually. Venkatachalam et al. [53] compared the mineralisation efficiency of 4-CP using lamps of wavelength 365nm and 254nm over TiO_2. The mineralisation rate at 365nm is reported to be slightly higher than at 254nm. Since the band gap excitation of electrons in TiO_2 with 254nm can promote electrons to the conduction band with high kinetic energy, they can reach the solid-liquid interface easily, suppressing the electron-hole recombination in comparison to 365nm. Chiou et al. [54] studied the effect of UV light intensity (20-400W) on the phenol degradation. All the reactions followed the first order kinetics. In the UV/TiO_2 system, the degradation rate constants with a light intensity of 20, 100, and 400W are 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. Increasing light intensity enhances the formation of hydroxyl radical thereby improving the degradation rate. Shukla et al. [34] studied the effect of light intensity (160-330 W) on the photocatalytic degradation of phenol using ZnO and artificial solar light. Under the conditions tested ($C_o=25ppm$, ZnO=0.4g/l, Persulfate=2g/l), the rate of degradation is shown to be favoured by the increase in lamp power with 95% conversion being obtained within 3h using the lamp power of 330W as opposed to 4h while using the lamp power of 160W. Han et al. [55] studied the photocatalytic degradation and mineralisation of 4-CP, hydroquinone and 4-nitrophenol (4-NP) using UV lamp emitting at 254 nm and VUV lamp emitting at both 254 and 185nm. VUV irradiation was reported to be efficient for the degradation of organics. This effect was attributed to the additional photons of 185nm and the higher energy of illumination with VUV lamps than with UV lamps. The order of TOC removal rate of each phenol was shown to be VUVPCD >VUVPD> UVPCD>UVPD, except for 4-NP under VUV irradiation which had no significant difference due to TiO_2 catalyst. The degradation rates in both processes are reported to follow the order: 4-CP> hydroquinone> 4-NP.

3.3 Initial concentration

Successful application of the photocatalytic oxidation system requires the investigation of the dependence of photocatalytic degradation rate on the substrate concentration. Hong et al. [56] examined the effect of initial concentration (50-400ppm) on the degradation of phenol over TiO_2 when the ratio of H_2O/titanium isopropoxide is 75. Highest degradation was observed at 50ppm initial concentration. Parida et al. [57] studied 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 found to decrease from 94% to 52% with increasing initial concentration. The degradation was reported to decrease from 95% to 50% under visible light. Shukla et al. [34] studied the effect of initial concentration (12.5-37.5ppm) on the degradation of phenol using UV-vis/ZnO/persulfate. Under the

conditions tested (ZnO=0.4g/l, persulfate=2g/l and power=330W), the degradation was highest at 12.5ppm. Parida et al. [58] examined the effect of substrate concentration on the degradation of 4-nitrophenol (20-100 mg/l). The amount of degradation was found to decrease from 100 to 40.9% as the initial substrate concentration increases from 20 to 100 mg/l. This is due to the absorption of light by the substrate at high concentration for the given catalyst loading. Priya et al. [33] examined the effect of initial concentration (10-76ppm) on the photocatalytic degradation of 2,4-dinitrophenol in the presence of combustion synthesised TiO_2 and P25. Maximum degradation was observed at 76ppm. Pardeshi et al. [59] reported that the degradation efficiency of phenol was shown to decrease as the phenol concentration increases from 25 to 300mg/l in the presence of ZnO and sunlight. When the concentrations of phenol are high, more and more phenol molecules are adsorbed on the surface of ZnO. In contrast, the relative number of ·OH and ·O^2- radicals attacking the phenol molecules decreases due to constant reaction conditions. As a result the photocatalytic degradation decreases. Venkatachalam et al.[53] examined the effect of initial concentration (50-300mg/l) on the photocatalytic degradation of 4-CP using nano TiO_2. The degradation rate was found to increase up to an initial concentration of 250mg/l and then decreased. The degradation follows pseudo-first order kinetics at low 4-CP. This is ascribed to the screening effect at concentrations greater than 250mg/l, and hence degradation efficiency decreased. Lathasree et al. [60] 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 the lower concentration range and it decreased with increase in concentration. The degradation was found to follow the first order kinetics. For chlorophenols, the initial rate was observed to increase with increase in the initial concentration range 40-60ppm and decreased with further increase in concentration. Barakat et al. [61] tested the effect of initial concentration(12.5-75ppm) on the photocatalytic degradation of 2-CP using 0.036 mol% Co-doped TiO_2. At a concentration of 12.5ppm, 2-CP can be totally decomposed within 3h. The degradation process follows a pseudo first- order reaction. The observed rate constant was shown to vary from 0.020 to 0.008min^{-1} as the concentration increases from 12.5 to 75mg/l. Kusvuran et al. [37] examined the effect of initial concentration (0.1-0.5mM) for the photocatalytic degradation of di and tri-substituted phenols using UV/TiO_2. The degradation rate constant of TCP was increased from 0.0372 to 0.0136min^{-1} under the conditions tested. For TBP and TMP, the degradation rate constant was shown to increase from 0.0252 to 0.0071 min^{-1} and 0.0153 to 0.0034min^{-1} respectively. TCP with the strongest electronegativity character of the compounds studied exhibits lower affinity to be adsorbed on TiO_2 catalyst. As a result of that, the number of reactive sites on TiO_2 increased and higher degradation levels were observed when initial TCP concentration was low. Chiou et al. [62] tested the effect of initial concentration (12.5-200 mg/l) on the photocatalytic degradation of phenol using 0.072mol% Pr-doped TiO_2. The highest degradation was 100% after 60 min irradiation for a range of concentration 12.5-25mg/l. The rate of degradation was shown to decrease as the phenol concentration increases from 50 to 200mg/l. Chiou et al. [63] studied the effect of initial concentration (15.3-83.5 mg/l) on the photocatalytic degradation of phenol and m-nitrophenol by UV/TiO_2 process. More than 90% of phenol is degraded within 60 min irradiation when the initial concentration is

15.3mg/l. However, 42% phenol is removed in 180 min when initial concentration increases up to 83.5mg/l. Under the identical conditions, 83% and 43% of m-NP is degraded at an initial concentration of 15.3 and 83.5mg/l, respectively. The limited number of surface sites on TiO_2 particles may control the photodegradation. As indicated in several investigations, as the concentration of target pollutant increase, more and more molecules of the compound get adsorbed on the surface of the photocatalyst. Therefore, the requirement of reactive species ($\cdot OH$ and $\cdot O_2^-$) needed for the degradation of pollutant also increases. However, the formation of $\cdot OH$ and $\cdot O_2^-$ 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 the pollutant degradation at higher concentrations. Consequently the degradation rate of pollutant decreases as the concentration increases [25]. 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 of the photocatalyst, and consequently result in a reduction in the degradation rate. In contrast, at low concentration the number of catalytic sites will not be a limiting factor, and the rate of degradation is proportional to the substrate concentration in accordance with apparent first-order kinetics [48,49]. Several investigations adequately described the dependence of photocatalytic degradation rates on the concentration of various phenols and dyes by the Langmuir-Hinshelwood (L-H) kinetics model [64-66]. The L-H model is used to describe the dependence of the observed reaction rate on the initial solute concentrations [67], although the model parameters will be strongly dependent on the composition of the effluent and other reactor operating conditions.

3.4 Catalyst loading

Several studies have indicated that the photocatalytic rate initially increases 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 surface area available for light absorption and hence a drop in 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 compromised because of excessive particle concentration. The trade off between these two opposing phenomena results in an optimum catalyst loading for the photocatalytic reaction [15]. 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 4 presents the influence of catalyst loading on the photocatalytic degradation of phenols. Parida et al. [58] studied the effect of ZnO concentration (0.2 to 2.0g/l) on the photocatalytic degradation of 4-nitrophenol under solar irradiation. At high concentration, the degradation rate was observed to have levelled off. Under the conditions tested, the degradation of 4-NP was found to increase with increase in ZnO loading up to 0.6g/l. An increase in the amount of catalyst provides an increased number of active sites for adsorption; however, the simultaneous increase in solution opacity causes a decrease in the penetration of

the photon flux. This suggests that the amount of photocatalyst to be used should maintain a balance between these two opposing effects. Selvam et al. [40] indicated that the degradation rate constant of 4-fluorophenol increases from 0.0152 to $0.0358\,min^{-1}$ as the concentration of TiO_2 increases from 50 to 150mg in the presence TiO_2 P25. Further increase in catalyst loading (150 to 250mg) results in a decrease in the rate constant from 0.0358 to $0.0296\,min^{-1}$. In the case of ZnO, a similar observation has been made. This was related to the aggregation of free catalyst particles and the screening effect resulting from the excessive opacity of the solution. The optimum concentrations were found to be 150mg TiO_2 and 200mg ZnO for efficient removal of 4-fluorophenol. The photodegradation efficiency of BPA was shown to increase when the dosage increased up to $100\,mg/200\,cm^3$, and then the efficiency was nearly 100% in the TiO_2 dosage range $100-600/200\,cm^3$ [68].

Table 4

Effect of catalyst loading on the photocatalytic degradation of various phenols

Pollutant	Light source	Photocatalyst	Tested catalyst loading (g/l)	Optimum loading (g/l)	Ref.
4-Nitrophenol	Solar	ZnO	0.2-2.0	0.6	[58]
Phenol	Solar	ZnO	0.5-3.5	2.5	[59]
4-Chlorophenol	UV	TiO_2	1.0-5.0	2.0	[53]
Phenol	UV	ZnO	1.0-3.0	2.0	[60]
2-Chlorophenol	UV	$Co-TiO_2$	0..005-0.03	0.01	[61]
Phenol	UV	TiO_2	1.0-4.0	2.0	[56]
Phenol	UV	$Pr-TiO_2$	0.-1.2	1.0	[62]

Pardeshi et al. [59] studied the effect of ZnO concentration (0.5 to 3.5 g/l) on the solar photocatalytic degradation of phenol. As the amount of ZnO increases, the number of phenol molecules adsorbed was also increased due to an increase in the number of ZnO particles. Thus the photocatalytic degradation was enhanced. Further increase in the amount of catalyst showed an adverse effect. Under the conditions tested, the highest degradation was observed at 2.5g/l of ZnO. The decrease in degradation beyond 2.5g/l is attributed to the screening effect of excess ZnO particles in the solution and scattering of light. Shukla et al. [34] observed an optimum concentration of 0.8g/l of ZnO for the solar photocatalytic degradation of phenol under a UV-vis/ZnO/persulfate system. For ZnO loading of 0.2g/L, the degradation efficiency of phenol is shown to be 95% at 4 h while a complete degradation is reached within 3 h for 0.4g/L or within 2 h at higher amounts of catalyst loading. In contrast to accelerating the rate of reaction resulting from the addition of excess catalyst, it can possibly cause a negative effect by reducing the light transmittivity due to the formation of an opaque solution. Venkatachalam et al. [53] tested the effect of catalyst loading (1-5g/l) on the photocatalytic degradation of 4-CP and observed an optimum catalyst concentration of 2.0g/l

for the degradation of 4-CP. At high catalyst loading, the reported low degradation rate is attributed to the deactivation of activated molecules through collision with ground state titania molecules. Lathasree et al. [60] examined the effect of ZnO on the photocatalytic degradation of phenols in the range of 1.0-3.0g/l. The optimum degradation was shown to be at 2.0g/l ZnO under the experimental conditions. The decrease in the degradation rate beyond catalyst loading of 2.0g/l was attributed to the screening effect of excess catalyst particles in the solution. Barakat et al.[61] studied the effect of 0.036mol% Co-doped TiO_2 concentrations (5-30mg/L) on the photocatalytic degradation of 2-CP. The degradation reached a maximum value of 93.4% with catalyst dosage of 10mg/L. However, a further increase in the catalyst dosage slightly decreased the degradation efficiency. Hong et al. [56] investigated the effect of catalyst dosage (1.0-4.0g/l) on the photocatalytic degradation of phenol. Under the conditions tested, optimum degradation was achieved at 2.0g/l. Chiou et al. [62] studied the effect of 0.072mol% Pr-doped TiO_2 concentration (0.2-1.2g/L) on the photocatalytic degradation of 50mg/l phenol. The degradation increases with increasing dosage of 0.072mol% Pr-doped TiO_2, and reaches a maximum of 96.5% at a dosage of 1.0g/L. However, a further increase in catalyst dosage to 1.2g/L, slightly reduces the photodegradation efficiency due to the decrease in light penetration by the suspension. In order to ensure uniform light intensity in the photocatalytic reactor, optimum catalyst loading must be determined.

3.5 Medium pH

Organic compounds 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 a pH below its pKa value, an organic compound exists as a neutral species. Above this pKa value, an organic compound attains a negative charge. Some compounds can exist in positive, neutral, as well as negative forms in aqueous solution. This variation can also significantly influence their photocatalytic degradation behaviour. The pH of the wastewater can vary significantly. The pH of an aquatic environment plays an important role on the photocatalytic degradation of organic contaminants since it determines the surface charge of the photocatalyst and the size of aggregates it forms [69-70]. The surface charge of a photocatalyst and 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 is strongly dependent on the pH of the solution. 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 their main structures [71]. 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:

$$\text{pH} < P_{zc} \quad \text{TiOH} + \text{H}^+ \dashrightarrow \text{TiOH}_2^+ \qquad (5.1)$$

$$\text{pH} > P_{zc} \quad \text{TiOH} + \text{OH}^- \dashrightarrow \text{TiO}^- + \text{H}_2\text{O} \qquad (5.2)$$

The point of zero charge (P_{zc}) of the TiO_2 (Degussa P25) is widely investigated/ reported at pH~6.25 [25]. 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. Table 5 shows the influence of pH on the photocatalytic degradation of various phenols. At pH 5-9, the Zn^{2+} and Fe^{3+} co-doped TiO_2 is found to show higher photoactivity for the degradation of phenol, whereas an optimal pH range of 3-4 was reported for the pure TiO_2 [72]. Venkatachalam et al. [53] studied the effect of pH (4-9) on the photocatalytic degradation of 4-CP (250mg/l) using nano TiO_2. The rate of degradation in the acidic pH range (at 5) was found to be higher than the alkaline pH. The high degradation rate in the acidic pH is due to enhanced adsorption of 4-CP on the surface of nano TiO_2 that carries positive charge.

Table 5

Influence of pH on the photocatalytic degradation of phenol and substitute phenols

Pollutant	Light source	Photocatalyst	Tested pH range	Optimum pH	Ref.
4-Nitrophenol	Solar	ZnO	2.0-7.0	6.0	[58]
Phenol	Solar	ZnO	3.0-11.0	5.0-7.0	[59]
4-Chlorophenol	UV	TiO_2	4.0-9.0	5.0	[53]
2-phenyl phenol	UV	ZnO	6.6-12.0	12.0	[73]
2-Chlorophenol	UV	Co-TiO_2	4.0-12.0	9.0	[61]
4-flurophenol	UV	ZnO/TiO_2	4.0-9.0	7.0	[40]
Phenol	UV	TiO_2	3.0-8.0	5.0	[74]
m-Nitrophenol	UV	TiO_2	4.1-12.7	8.9	[63]
4-Chlorophenol	UV	N-TiO_2	2.0-5.0	3.0[a]	[75]

[a] precursor solution pH

In the acidic pH, minimisation of electron-hole recombination is also an important factor for the enhanced degradation of 4-CP. In alkaline pH (at 9), the degradation rate was found to be less due to the negative charge of nano TiO_2 and 4-CP. Parida et al. [58] examined the effect of pH (2-7) on the photocatalytic degradation of 4-NP. The degradation rate was found to increase 92% at pH 6.0 and thereafter decreased with increasing pH of the solution. At pH 6, the surface charge of ZnO can attract the largest amount of negatively charged anions of 4-nitrophenol. At pH above 7, negative charges predominate on the surface of ZnO which hinders the degradation of 4-NP. Pardeshi et al. [59] investigated the effect of pH (3-11) on the solar photocatalytic degradation of phenol using ZnO suspension. Under the conditions tested, the highest degradation was achieved at pH 5-7. At pH 5-7, most of the phenol remains undissociated, hence the

maximum number of phenol molecules are adsorbed on the ZnO surface and consequently result in enhanced photodegradation. In an alkaline medium, the ZnO surface is negatively charged and phenolate intermediates may be repelled away from the ZnO surface which opposes the adsorption of substrate molecules on the surface of the catalyst. As a result, phenol degradation decreases in alkaline medium. Using ZnO, Lathasree et al. [60] studied the effect of pH (3.5-9) on the photocatalytic degradation of phenol, o-chlorophenol and p-chlorophenol. The phenol degradation was reported to be favourable in mild acidic and neutral solutions. However, o-chlorophenol and p-chlorophenol was found to undergo degradation at a faster rate at lower pH values. This behaviour is attributed to the undissociated state of the chlorophenol species in acidic conditions which favours its adsorption on the ZnO surface. At high pH, chlorophenols exist as negatively charged anions which weaken its adsorption due to electrostatic repulsion between catalyst and anions. Khodja et al. [73] examined the effect of pH (6.6-12) on the photocatalytic degradation of 2-phenyl phenol using ZnO. The degradation efficiency was shown to be greater at higher pH due to the abundance of hydroxyl radicals or to the anionic form of the tested compound to be oxidized compared to its molecular form. Barakat et al. [61] investigated the effect of pH (4-12) on the photocatalytic degradation of 2-CP using 0.036 mol% Co-doped TiO_2. At lower pH (4-7), the degradation efficiency was significantly less as compared to higher pH, with a maximum value of 93.4% at pH 9. They reported that higher concentrations of hydroxyl ions are available at higher pH values to react with the holes to form hydroxyl radicals ($\cdot$OH), thereby enhancing the photodegradation of 2-CP. Further increase in pH indicated only a small increase in the photodegradation efficiency. Selvam et al. [40] studied the effect of pH (4-7) on the photocatalytic degradation of 4-FP. After 30 min irradiation, the pseudo-first order rate constants were 0.0233, 0.0370 and 0.028min^{-1} for P25 and 0.0213, 0.0325 and 0.0231min^{-1} for ZnO at pH 4, 7 and 9 respectively. Since the pKa of 4-flurophenol is 9.89, it exists as molecular form for the tested pH range. As a result, higher adsorption and consequently higher degradation are reported to be observed at neutral pH for both catalysts. In the presence of P25 and ZnO, the effect of pH on the photocatalytic degradation of 4-fluorophenol was observed to be pH 7> pH 9> pH 4. Akbal et al. [74] examined the effect of pH (3-8) on the photocatalytic degradation of phenol. At low pH degradation of phenol was rapid, and the highest degradation (70.3%) was achieved at pH 5. The addition of H_2O_2 to the UV/TiO_2 system was observed to enhance the phenol degradation to 99.2%. Chiou et al. [63] studied the effect of pH (4.1-12.7) on the photocatalytic degradation of phenol and m-NP (C_o=0.51mM, TiO_2=1g/l). The degradation efficiency is above 65% within 180 min with the pH lower than 11; however, it reaches 53% at pH 12.7. The degradation is over 85% within 180 min for m-NP, and the degradation was more effective in neutral and weakly alkaline media. The degradation decreases in the order pH 8.9>pH 7> pH11. In neutral to weak alkaline media, TiO- is the predominant group on TiO_2 particles, and phenols are primarily present in the molecular forms. Both of them combined by hydrogen bonding simply, and thus increased the amount of adsorption and enhanced the photodegradation rate. Yu et al. [75] tested the influence of a precursor solution pH (2.0-5.0) on the photocatalytic activity of N-TiO_2 calcined at 500°C for the degradation of 4-CP. The efficiency of N-doped TiO_2 was found to increase as the pH

decreased from 5.0 to 3.0. Further decrease in pH to 2.0 affected the photocatalytic activity of the catalyst negatively. Hence, the optimum pH for that particular catalyst's preparation was 3.0. A possible reason for the adverse effect on the photocatalyst performance at low pH is that the increased of H^+ concentration may restrain hydrolysation of Ti(OBu)4 and thereby reduce the crystal size of the prepared N-doped TiO_2 nanoparticles. In sum, different phenols have different activity in photocatalytic reaction. Some are degraded faster in acidic pH, while others degrade faster at higher pH. All these effects can be attributed to the nature of the pollutant to be degraded. Thus, it is important to study the nature of the pollutants to be degraded, and determine the optimum pH.

3.6 Co-occurring Substances

The amount of UV absorption is influenced by water transmittance over the spectral UV range of interest. Some common constituents that affect water transmittance are dissolved organic matter, nitrate and ferrous/ ferric ions. The presence of "spectator's components" in water can affect adversely the contaminant degradation rates. Inorganic anions, such as phosphate, sulphate, nitrate, and chloride, have been reported to limit the performance of solar based photocatalysis [76]. Bicarbonate in particular is detrimental to reactor performance as it acts as a hydroxyl radical scavenger [76]. Long time experience with photocatalytic oxidation systems showed that humic substances in contaminated water can strongly adsorb titanium dioxide particles and reduce activity toward the target substances [77]. Lin et al. [78] observed that the presence of humic acid caused a significant retardation on the photocatalytic degradation of 4-chlorophenol. The observed retardations of humic acids were 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 transmission, and therefore the photooxidation rate. Humic acid can also compete with organohalides for the active sites on the TiO_2 surface.

Popadam et al. [79] examined the effect of the water matrix on the decolourisation of acid orange 20. The presence of 5g/l NaCl and Na_2SO_4 led to decreased decolourisation which was attributed to the trapping of photo generated valence band holes and the hydroxyl radicals by the respective anions. Aarthi et al. [80] investigated the effect of metal ions (Cu^{2+},Fe^{3+},Zn^{2+}, and Al^{3+}) on the photocatalytic degradation of Rhodamine B which was shown to follow the order of Cu^{2+}>Al^{3}> Zn^{2}>Fe^{3+}. In the presence of Cu^{2+} and Zn^{2+}, the degradation of Malachite Green was reduced by 76 and 66% respectively. In the presence of metal ions, the surface of TiO_2 is modified due to the adsorption of cations or anions. The effect of metal ions on the photocatalytic degradation rates is attributed to the suppression of $\cdot$OH radicals due to trapping of the conduction band electrons by the adsorbed metal ions. Khodja et al. [73] examined the effect of sodium chloride, sulphate and nitrate concentration on the photocatalytic degradation of 2-phenyl phenol. A large amount of these anions is shown to affect negatively the degradation rate. This inhibition can be attributed to a competitive adsorption on the ZnO of these anions and molecules of substrate. Selvam et al.

[40] examined the effect of transition metal ions on the photocatalytic degradation of 4-flurophenol which was shown to be in the order of $Mg^{2+}>Fe^{2+}>Fe^{3+}>>Cu^{2+}$ in an acidic medium, whereas the trend was observed to be $Mg^{2+}>Fe^{3+}>Cu^{2+}>Fe^{2+}$ in a basic medium. The enhancement of degradation in the presence of these ions except Cu^{2+} is due to the increase of charge separation by accepting the conduction band electrons. The inhibition of inorganic anions on the degradation of 4-FP was demonstrated to be $CO_3^{2-}>HCO_3^->Cl^->NO_3^->SO_4^{2-}$. The main inhibition from these anions is attributed to their adsorption on the TiO_2 surface. Addition of CO_3^{2-}, HCO_3^- and Cl^- ions decreases degradation of 4-flurophenol due to the hydroxyl radical quenching by these ions. The SO_4^{2-} ions react with hydroxyl radicals to form $SO_4^{\cdot-}$ ions. The sulphate radical anion can accelerate the reaction, and no quenching was observed for the NO_3^- ion. Naeem et al. [81] studied the inhibition effect of anions on the photocatalytic degradation of phenol. The order of effects was demonstrated to be $Cl^->SO_4^{2-}>NO_3^->CO_3^{2-}$. This is due to the fact that the Cl^- ions act as radical scavengers, and can react with hydroxyl radicals to form $\cdot Cl_2$ or $\cdot ClOH^-$ which may retard the photocatalytic oxidation reaction dramatically. But the inhibitive effect of SO_4^{2-} can be attributed to the competitive adsorption of SO_4^{2-} and the target organic compound on the catalyst surface. At certain concentrations, Fe^{3+} is reported to improve the degradation rate whereas Ca^{2+}, Cu^{2+}, and Mg^{2+} hinder the degradation process. The improvement in degradation with Fe^{3+} addition is due to the electron scavenging effect that prevents the recombination of electrons and holes which favours the formation of $\cdot OH$ and $O_2^{\cdot-}$ on the TiO_2 surface. The decrease in degradation in the presence of other metal ions is attributed to low reduction potential. The effect of surfactants (0.05mM/L) on the degradation rate of phenol was reported 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, therefore influencing the catalytic activity and hence the photocatalytic degradation.

Organic solvents are mostly present in many industrial wastewaters. As a result, their effects on the photocatalytic degradation system have been investigated in several studies. Lin et al. [78] examined the effects of acetonitrile or isopropanol on the photocatalytic oxidation of 4-Chlorophenol. The degradation rate of 4-Chlorophenol was shown to decrease from $1.0436h^{-1}$ to $0.0525h^{-1}$ as the acetonitrile content increases in the reaction mixture. A similar retardation effect was also observed when 5% isopropanol was added into the acetonitrile: water (1:1) reaction mixture. Daneshvar et al. [82] studied the effect of ethanol (0-9% v/v) addition on the photodegradation of Acid Orange 7 in the presence of ZnO. Under the conditions examined, the addition of ethanol inhibited the degradation of AO7 due to $\cdot OH$ competitive reactions with AO7 and ethanol. Thus, the incorporation of a pre-treatment process has been indicated to have a beneficial effect on the performance of photocatalytic oxidation.

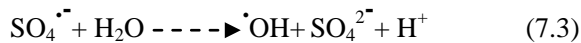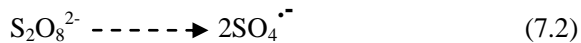### 3.7 Oxidants/electron acceptor

The electron/hole recombination is one of the main drawbacks in the application of TiO_2 photocatalysis as it causes a 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 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 by (1) removing the electron-hole recombination by accepting the conduction band electron; (2) increasing the hydroxyl radical concentration and oxidation rate of intermediate compounds; and (3) generating more radicals and other oxidizing species to accelerate the degradation efficiency of intermediate compounds [25-32]. Since hydroxyl radicals appear to play an important role in the photocatalytic degradation, several researchers have investigated the effect of the addition of electron acceptors such as H_2O_2, $KBrO_3$, and $(NH_4)_2S_2O_8$ on the photocatalytic degradation of various organic compounds [26-32] 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 rates compared to molecular oxygen. In most of the cases, the order of enhancement is reported to be $UV/TiO_2/H_2O_2 > UV/TiO_2/BrO_3^- > UV/TiO_2/S_2O_8^{2-}$. The enhancement of degradation rate is due to the reaction between BrO_3^- and conduction band electrons. This reaction reduces the recombination of electron-hole pairs.

$$BrO_3^- + 6e_{CB}^- + 6H^+ \dashrightarrow Br^- + 3H_2O \qquad - (7.1)$$
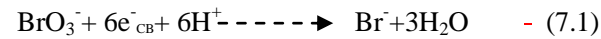
$S_2O_8^{2-}$ can generate sulphate radical anion ($SO_4^{\bullet -}$) both thermally and photolytically in aqueous solution. $SO_4^{\bullet -}$ then reacts with H_2O to produce $^{\bullet}OH$ radicals.

$$S_2O_8^{2-} \dashrightarrow 2SO_4^{\bullet -} \qquad\qquad (7.2)$$

$$SO_4^{\bullet -} + H_2O \dashrightarrow {}^{\bullet}OH + SO_4^{2-} + H^+ \qquad (7.3)$$

With the addition of H_2O_2, the enhancement of degradation is due to the increase in the hydroxyl radical concentration as shown by Eqs. (7.4) and (7.5);

$$H_2O_2 + e_{CB}^- \dashrightarrow {}^{\bullet}OH + OH^- \qquad (7.4)$$

$$H_2O_2 \dashrightarrow {}^{\bullet}OH + {}^{\bullet}OH \qquad\qquad (7.5)$$
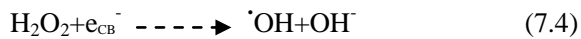
The degradation efficiency of the UV/TiO$_2$/oxidant process is slightly more in an acidic medium than in a basic medium. Selvam et al. [40] studied the effect of oxidants on the photocatalytic degradation of 4-flurophenol which was shown to be in the order of $IO_4^- > BrO_3^- > S_2O8_2^- > H_2O_2 > ClO_3^-$. After 15 min irradiation at pH 4, the degradations of 4-flourophenol were observed to be 79.86%, 66.89%, 60.88%, 53.85% and 46.35% in UV/TiO$_2$/IO$_4^-$, UV/TiO$_2$/BrO$_3^-$, UV/TiO$_2$/H$_2$O$_2$, UV/TiO$_2$/S$_2$O$_8^{2-}$ and UV/TiO$_2$/ClO$_3$- processes respectively. IO$_4$- was found to be the most efficient oxidant due to the generation of a number of highly reactive intermediate radicals such as IO$_3^{\bullet}$, OH$^{\bullet}$ and IO$_4^-$. The same trend is also observed in both acidic and basic mediums for the UV/ZnO/oxidant process. However, the UV/TiO$_2$/oxidant process is slightly more efficient than the UV/ZnO/oxidant process. The higher

efficiency of BrO_3^- than $S_2O_8^{2-}$ is due to the electron scavenging effect of BrO_3^-. Under visible light irradiation, the influence of oxidants on the degradation of Acid Red 88 by $Ag-TiO_2$ was found to be peroxomonosulfate> peroxodisulfate> hydrogen peroxide [83]. The addition of 50ml H_2O_2 to a 1.00mM p-dihydroxybenzene solution was reported to increase the removal efficiency from 37 to 80% after 200 min reaction time due to the high oxidising capacity of hydroxyl radicals [84]. Chiou et al. [54] investigated the effect of H_2O_2 addition from 1.77 to 88.2mM on the photocatalytic degradation of phenol. The addition of H_2O_2 from 1.77 to 8.82mM leads to an increase in removal efficiency from 58 to 84% within 3h. In contrast, phenol is completely degraded within 2.5 and 1h when the level of H_2O_2 increases to 44.1 and 88.2mM respectively.

3.8 Calcination temperature

Structure and size of TiO_2 crystallites are significantly dependent on calcination temperatures. Thermal treatment of TiO_2 gels at higher temperatures promotes phase transformation from thermodynamically metastable anatase to the more stable and condensed rutile phase. As the dehydration process occurs during heat treatment, crystallites grow to dimensions larger than those of the original particles. Table 6 shows the influence of calcination temperatures on the photocatalytic degradation of various phenolic compounds. Nanocrystalline titanium oxide powder for catalytic purposes can be applied by a variety of techniques including sol-gel method, solvo-thermal process, reverse micellar, hydrothermal method and electrochemical methods. An et al. [85] studied the effect of calcination temperatures (350-650°C) on the photocatalytic degradation of 2,4,6-tribromophenol (TBP) using mesoporous-TiO_2 prepared by hydrothermal assistant sol-gel method. The TBP degradation rate constant was found to increase from 0.010 to 0.018min^{-1} when calcination temperature was increased from 350 to 550°C. A sharp decrease in the rate constant to 0.004min^{-1} was observed when the sample was thermally treated at 650°C. As the treatment temperature increases from 350 to 550°C, the resulting TiO_2 increases its crystallite size from 9.8 to 18.4nm, while BET surface area deceased from 142 to 49m^2/g. The increased photocatalytic degradation efficiency was attributed to the increased crystallinity. The decrease in photocatalytic degradation efficiency at 650°C was ascribed to the completely collapsed mesoporous structure of TiO_2. Pecchi et al. [86] investigated the effect of calcination temperatures on the photocatalytic degradation of pentachlorophenol using the sol-gel method under the pH range 3-9. The degradation rate constant was shown to increase from 6.9x10^3 to 7.9x10^{-3}min^{-1} and 7.0x10^{-3} to 10.1x10^{-3} min^{-1} respectively for pH values 3 and 5 as the calcination temperatures increased from 300 to 500°C. Nonetheless, the rate constant was higher at 300°C and 500°C compared that for 400°C at pH 9. Increasing calcination temperature results in reduced surface area from 175 to 67m^2/g at pH 3 and 170 to 68m^2/g at pH 5, and increased crystallinity and particle size from 3.3 to 8.7nm at pH 3 and 4.0 to 9.8nm at pH 9. No significant changes in the anatase and rutile proportion are observed as the calcination temperature increases. Gorska et al. [87] studied the effect of calcination temperatures (350°C-750°C) on the photocatalytic degradation of 0.21 mM phenol under UV (25<λ<400nm) and visible (λ>400nm) light irradiation. After 60 min irradiation, the maximum

amount of phenol degradation was about 80% when P25 TiO_2 was calcinated at 350^oC in the visible light. In addition to the largest BET surface area ($205.8 m^2/g$) and the smallest crystallite size (8.4nm) and average pore diameter (8.3nm) of TiO_2, this effect was attributed to the efficient absorption of light vis region due to the existence of the largest amount of carbon in aromatic C-C bonds (10.1 at%). However, the photocatalyst calcinated at 450^oC was found to have the highest activity in UV light irradiation. Silveyra et al. [88] tested the effect of calcination temperatures ($600-800^oC$) on the photocatalytic degradation of phenol using N-doped TiO_2 P-25. Highest degradation was obtained at 600^oC and no variation was observed at 700^oC and 800^oC. No discernible change in anatase to rutile ratio is noticed for N_2-doped TiO_2 at 600^oC whereas this ratio is beginning to be noticeable at 700 to 800^oC. Liqiang et al. [89] observed that the rutile phase began to appear when the pure TiO_2 samples calcinated at 600^oC, and the anatase phase disappeared when the calcination temperature was at 700^oC. In contrast a little rutile phase appeared in the La-doped TiO_2 samples when the sample was calcinated at 700^oC, and even most was shown to be anatase phase at a calcination temperature of 800^oC. A certain temperature,600^oC was reported to be the optimum calcination temperature for the highest photocatalytic degradation of phenol using 5 mol% La-doped TiO_2. Wawrzyniak et al. [90] studied the effect of calcination temperatures (100-800^oC) on the photocatalytic degradation of phenol and two azo dyes (reactive Red, direct Green) by N doped-TiO_2 under visible light irradiation. The highest effectiveness of phenol degradation was achieved at a calcination temperature of 700^oC. In the case of degradation of both of the azo dyes, the highest degradation was observed at 500^oC and 600^oC.

Table 6

Influence of calcinations temperature on the photocatalytic degradation of phenols

Pollutant	Light source	Photocatalyst	Range of calcination temperature	Optimum calcination temperature	Ref.
Phenol	UV	TiO_2 P-25	$350-750^oC$	350^oC	[87]
	Visible	TiO_2 P-25	$350-750^oC$	450^oC	[87]
Phenol	Visible	N_2-TiO_2	$600-800^oC$	700^oC	[88]
Phenol	UV	La- TiO_2	$600-800^oC$	600^oC	[89]
Phenol	Solar	Au-TiO_2	$275-500^oC$	275^oC	[91]
p-chlorophenol	UV	TiO_2	$300-500^oC$	500^oC	[86]
4-CP	UV	Zr^{4+}-TiO_2	$105-1100^oC$	900^oC	[92]
Phenol	UV/Visible	I-TiO_2	$400-600^oC$	400^oC	[93]
Phenol	Visible	N_2-TiO_2	$350-500^oC$	400^oC	[94]
2,4,6-TBP	UV	TiO_2	$350-650^oC$	550^oC	[84]
Phenol	UV	Pr-TiO_2	$100-800^oC$	600^oC	[62]

Cheng et al. [95] studied the effect of calcination times (0.5-3h) on the photocatalytic degradation of 4-CP using carbon modified TiO_2 calcinated at 350^oC under visible light irradiation. The surface area of synthesised TiO_2 decreases from 257 to $119m^2/g$ and the crystallite size increases from 4.35 to 5.58nm as the calcination times increase from 0.5 to 3.0 h. The catalyst calcinated for 1h is shown to have higher photocatalytic activity than the catalyst calcinated for 0.5h. The higher activity of the catalyst calcinated for 1h is due to its enhanced crystallization in anatase TiO_2 which acts as the recombination centres for photogenerated electrons and holes. Nonetheless, calcination time of more than 1h results in reduced photocatalytic activity due to the decrease of carbonaceous residues and surface area. Shaktivel et al. [96] studied the effect of calcination temperatures ($400-600^oC$) on the photocatalytic degradation of 4-CP under visible light irradiation ($\lambda \geq 455nm$) using a nitrogen-doped TiO_2 prepared by $TiCl_4$ hydrolysis in tetrabutylammonium hydroxide. A sample calcinated at 400^oC for 1h is reported to show 70 % TOC reduction of 0.25mM 4-CP. Porter et al. [97] examined the micro-structural changes in Degussa P-25 due to heat treatment. The TiO_2 powder was annealed from 600 to 1000^oC. Under UV irradiation, the apparent crystallite size and rutile content of the catalyst increased with increasing calcination temperatures, whereas the specific surface area and the rate of phenol degradation was reported to decrease. Sonawane et al. [91] tested the effect of calcination temperatures ($275-500^oC$) on the photocatalytic activity of 2%-Au/TiO_2 for the degradation of phenol under solar light. The catalyst calcinated at 275^oC exhibited the highest activity compared to the samples calcinated at higher temperatures. This effect is attributed to the formation of the most active pure anatase phase at this temperature and the particle size. At lower temperatures the particle growth will be limited to the surface area and the number of active sites will be more, hence the photocatalytic activity obtained is more than for prepared Au/TiO_2 and catalyst calcinated at higher temperatures.

Zhang et al. [43] studied the effect of calcination temperatures ($300-900^oC$) on the photocatalytic degradation of MO using $ZnO-SnO_2$. At 350^oC, the higher photocatalytic activity of coupled oxides was reported due to variation in phase composition and particle size. Using Z_2S as the catalyst, an optimum temperature of 600^oC was found for the degradation of MO [44]. Lukac et al. [92] studied the effect of annealing temperature ($105-1100^oC$) on the photocatalytic activity of Zr-doped TiO_2 for the degradation of 4-chlorophenol. The catalysts annealed between 800 and 900^oC are reported to be more efficient compared to the standard Degussa P25. The optimum size of the Zr-doped anatase crystallites is 69.2 and 86.5nm obtained at 875 and 900^oC respectively. The photocatalyst annealed at 900^oC was reported to have a 1.5 times higher degradation rate than the standard TiO_2 P25. The most photoactive catalyst annealed at 900^oC was shown to have 87wt.% of anatase and 13wt.% of rutile. Barakat et al. [61] studied the effect of annealing temperatures ($100-800^oC$) on the efficiency of 0.036 mol% co- doped TiO_2 for the photocatalytic degradation of 2-CP. The sample annealed at 800^oC is found to have rutile structure and shows lower degradation efficiency compared to the one annealed at 600^oC with anatase phase. The enhanced photoreactivity is attributed to the small particle size of TiO_2 (about 25nm) with a large surface area. The

band gap energy measured for this anatase sample was 3.2eV, which is identical to that of the bulk TiO_2. Hong et al. [93] examined the effect of calcination temperatures (400-600°C) on the photocatalytic degradation of phenol under UV and visible light irradiation (λ>400nm) using I-doped TiO_2 with anatase phase. Of the temperatures tested, I-doped TiO_2 calcinated at 400°C shows significantly higher photocatalytic activity compared to undoped TiO_2 nanoparticles (P-25 and pure TiO_2). Wang et al. [94] tested the effect of calcination temperatures (350-500°C) on the photocatalytic activity of N_2-doped TiO_2 with anatase phase for the degradation of phenol with visible light (λ>400nm). Under the conditions tested, mineralisation of phenol was significantly higher at 400°C due to its smaller particle size and higher adsorption area toward the organic substrate. Hong et al. [56] examined the influence of calcination temperatures (200-700°C) on the photocatalytic degradation of phenol using TiO_2 prepared by the sol-gel method. Under the experimental conditions, the maximum degradation was observed at a calcination temperature of 400°C with anatase phase TiO_2. The degradation of phenol decreases drastically above 600°C which was attributed to increased crystallite size and rutile phase of titania. Lv et al. [98] studied the effect of calcination temperatures (200-800°C) on the photocatalytic degradation of phenol using pure anatase and rutile TiO_2 in aqueous suspension, in the absence and presence of NaF. Under the experimental conditions (Anatase TiO_2=1.0g/L, pH=3), the maximum photocatalytic degradation rate was shown to be at 600°C under UV irradiation (λ>320nm). However, the degradation rate was retarded in the presence and absence of NaF when rutile TiO_2 was used. XRD analysis revealed that the rutile phase appears at calcination temperatures up to 700°C,and almost all the anatase crystallizes to rutile at 800°C. As the calcination temperature increased, the particle sizes of both anatase and rutile increased according to the diffraction intensity.

Chiou et al. [62] examined the efficiency of 0.072mol% Pr-doped TiO_2 for the photocatalytic degradation of phenol over a range of calcination temperatures from 100-800°C. XRD patterns indicated that the samples annealed at 100-400°C become crystalline with dominantly anatase structure. Upon annealing at 500-600°C, the samples possess both anatase and rutile structures, whereas the samples annealed at 800°C are completely transformed to the rutile structure. The highest degradation is achieved with samples annealed at 600°C (BET=40m^2/g) compared to the samples annealed at 800°C. There have been several investigations on photocatalytic degradation of various dyes by titania nanoparticles, however, information on the titania film fabrication routes on the photocatalytic degradation of dyes is still desirable. Song et al. [99] investigated the effect of titania films with different nanostructures of nanorods (NR), sol-gel film (SG), nanotubes (NT) and nanoparticle aggregates (DP) 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, and the order was shown to be NR>SG>DP>NT for the degradation of MB. An order of NT>DP>SG>NR was observed for the degradation of MO. The loss of TiO_2 nanoparticle surface area throughout the growth of nanocrystallites during high temperature calcination (>400°C) and serious aggregation of prepared nanoparticles when dispersed in aqueous solution need to be addressed to achieve further progress.

3.9 Doping and mixed semiconductor

The recombination of photogenerated electrons and holes is the reason behind the low photoactivity of TiO_2. Structural imperfections in the TiO_2 lattice generate trap sites which may act as recombination centres, leading to a decrease in the levels of electrons and holes. In order to enhance the TiO_2 photocatalysis as well as the response into the visible spectrum of solar light, TiO_2 has been doped with certain transition metals, non-metals and ionic components. Doped ions can also act as charge trapping sites and thus reduce electron-hole recombination. The effect of doping on photocatalytic activity is governed by several factors, e.g. the type and concentration of dopant, preparation method, the structure and the initial concentration of the pollutants (phenols and its derivatives), and physico-chemical properties of the catalyst. Both positive and negative results have been reported from doping with metal ions. The increase in charge separation efficiency will enhance the formation of both free hydroxyl radicals and active oxygen species [100]. Table 7 shows the influence of doping on the photocatalytic degradation of various phenolic compounds. Kirilov et al. [101] studied the efficacy of Ag and Pd modified TiO_2 prepared by impregnation method for the photocatalytic degradation of p-chlorophenol. Under the conditions tested, complete degradation is achieved after 180 min reaction in the case of 0.5% Ag/TiO_2 and 0.1% Ag/TiO_2. For 0.25% Ag/TiO_2, the complete degradation is observed after 240 min. In contrast, 90% degradation is obtained with unmodified TiO_2. Similar trends have also been observed for 0.1% Pd/TiO_2 and 0.5% Pd/TiO_2.

Table 7

Influence of doping concentration on the photocatalytic degradation of various phenols

Pollutant	Light source	Photocatalyst	Doping (%)	Optimum doping(%)	Ref.
Phenol	Visible	Fe^{3+}-TiO_2	0.4-5.1	1.0	[102]
4-Chlorophenol	Visible	Ce-TiO_2	0-1.0	0.6	[103]
2,4-Dichlorophenol	Visible	V-TiO_2	0.25-5.0	1.0	[104]
p-chlorophenol	UV	Ag-TiO_2	0.1-0.5	0.5	[101]
p-chlorophenol	UV	Pd-TiO_2	0.1-0.5	0.5	[101]
Phenol	UV	Fe^{3+}-TiO_2	0-3.0	0.5	[105]
4-Chlorophenol	UV	Zr^{4+}-TiO_2	0.5-5.0	3.0	[106]
2-Chlorophenol	UV	Co-TiO_2	0.004-0.14	0.036	[61]
Phenol	UV	La-TiO_2	1.0-5.0	1.0	[89]
Phenol	UV	Pr-TiO_2	0-0.22	0.072	[62]
2,4,6-Trichlorophenol	UV-A	Ag-TiO_2	0-2.0%	0.5	[107]

Comparatively Ag/TiO$_2$ samples showed higher photocatalytic activity than Pd/TiO$_2$. In comparison to unmodified TiO$_2$, the improved activity of Ag and Pd modified TiO$_2$ is attributed to better charge separation and consequently, to slower recombination. Rengaraj et al. [107] investigated the photocatalytic activity of Ag-TiO$_2$ prepared by the sol-gel method for the degradation and mineralisation of 2,4,6-trichlorophenol (TCP) in aqueous solution under UV-A illumination. In Ag-doped TiO$_2$, the Ag content is varied from 0.1 to 2.0wt%. Degradation of TCP is demonstrated to be more than 95% within 120 min, and the corresponding TOC reduction is reported to be 80 % in 120 min. The kinetics of TCP degradation follows a pseudo-first-order kinetic. The 0.5%Ag-TiO$_2$ catalyst is shown to have the highest efficiency for the degradation of 2,4,6-TCP. The degradation rate constant is reported to be 0.1046 min^{-1} for 0.5%Ag-TiO$_2$ compared 0.0682 min^{-1} for undoped TiO$_2$. The photocatalytic activity enhancement due to Ag doping is related to better separation of photogenerated charge carriers and improved oxygen reduction inducing a higher extent of degradation of aromatics. Arabatzis et al. [108] observed a two times faster degradation of methyl orange in the presence of Au/TiO$_2$ thin films compared to that obtained with the original TiO$_2$ material. TiO$_2$ with gold surface coverage of 0.8μg cm^{-2} is shown to be more efficient for photocatalysis. The improvement in the efficiency is reported to be more than 100%. This enhancement is attributed to the presence of Au particles which attract conduction band electrons and prevent electron-hole recombination.

Sonawane et al. [91] tested the effect of Au doping (1-2%Au/TiO$_2$) on the photocatalytic degradation of phenol in solar light irradiation of 4.5-5Wm^2/day. In comparison to undoped TiO$_2$, TiO$_2$ doped with 1-2%Au showed 2-2.3 times higher photocatalytic activity. The degradation rate constant of pure TiO$_2$ was 0.004945min^{-1}, whereas the rate constants of 1%Au/TiO$_2$and 2%Au/TiO$_2$ were 0.01041min^{-1} and 0.01128min^{-1}, respectively. The increase in photocatalytic activity of Au-doped TiO$_2$ films was observed. This increase is attributed to the combined effect of shift in absorption wavelength to visible, the shift in Fermi level to more negative potentials and improved efficiency of the interfacial charge transfer process. Using the sol-gel method, Venkatachalam et al. [106] examined the effect of Zr^{4+} doping (0.5-5.0mol% Zr^{4+}) onto TiO$_2$ matrix for the photocatalytic degradation of 4-Chlorophenol. The photocatalytic activity of 3.0mol% Zr^{4+}-doped TiO$_2$ samples were reported to be higher than that of nano TiO$_2$ and Degussa P25. Enhanced adsorption of 4-CP over the catalyst surface and the decrease in particle size are indicated to be the reason for high activity of the catalyst. The entry of Zr^{4+} into the lattice of TiO$_2$ creates charge compensating anion vacancies in the lattice points of TiO$_2$ which may enhance the adsorption of 4-CP. Zr^{4+}-doped TiO$_2$ contains only anatase phase whereas pure TiO$_2$ contains both anatase and rutile phase together. The incorporation of Zr^{4+} into TiO$_2$ led to small grain size, large surface area and high band gap values. This also led to the formation of more electron capture traps which contribute to high separation efficiency of photogenerated carriers. Burns et al. [109] have studied photodegradation of 2-chlorophenol using sol-gel synthesized Nd-doped TiO$_2$ under UV irradiation. They reported that doping TiO$_2$ with Nd^{3+} reduces the degradation time because of the difference in the ionic radii of Nd^{3+} and Ti^{4+}. Much larger substitutional Nd will cause localised charge perturbation and formation of oxygen vacancies which act as electron traps.

Bellardita et al. [110] investigated the effect of metal loading (W, Co and Sm) onto a TiO_2 matrix on the photocatalytic degradation of 4-nitrophenol. The photocatalytic activity of the samples with increasing metal loading is shown to increase until a maximum value and afterwards decreases. In comparison to Degussa P25, TiO_2 loaded with 1% W and Sm showed a significant improvement in the photocatalytic activity under UV irradiation, whereas Co is reported to be beneficial only under visible light irradiation. This effect was ascribed to an increased charge separation of the photogenerated electron-hole pairs in the presence of dopant ion. Sobana et al. [111] studied the effect of activated carbon (AC) content onto ZnO for the photocatalytic degradation of 4-acetylphenol in the presence of UV irradiation. Bare ZnO gives a complete disappearance of 4-AP in about 240 min of UV irradiation. In contrast, 9AC-ZnO removes 4-AP completely from the solution within 150 min due to a synergistic effect between ZnO and activated carbon. The distribution of ZnO is found to be more homogeneous in 9AC-ZnO compared to other AC-ZnO catalysts. 9AC-ZnO is found to be more efficient in solar light than in UV light.

Wang et al. [112] studied the Ag-doped ZnO for the photocatalytic degradation of MB by varying the doping ratio of Ag/Zn from 0 to 2%. Under the conditions tested, Ag doping significantly improved the photocatalytic activity of ZnO due to O vacancies, crystal deficiencies and increased specific surface area. Barakat et al. [61] studied the effect of Co (0.004-0.14mol%) doping onto TiO_2 nanoparticles by a sol-gel technique from $TiCl_4$ for the photocatalytic degradation of 2-Chlorophenol. The photocatalytic degradation efficiency of 0.036mol% Co-doped TiO_2 was shown to be 75.4% higher compared to undoped TiO_2 under the conditions tested. A further increase in Co concentration to 0.14mol% resulted in a decrease in the degradation efficiency to 83%.They reported that catalyst samples with 0.036mol% Co particles annealed up to 400^oC were amorphous, and became crystalline with dominantly anatase structure upon annealing at 600^oC. Under irradiation, Co(III) ions in the Co-doped TiO_2 work as electron scavengers which may react with the superoxide species and prevent the hole–electron recombinations and consequently increase the photo degradation efficiency. Herrera et al. [113] tested the photocatalytic activity of N,S co-doped and N-doped commercial anatase TiO_2 powders for the degradation of phenol under simulated solar irradiation. Undoped P25 was shown to have the highest photocatalytic activity. N,S co-doped powders showed almost the same photocatalytic activity as undoped TKP 102 (Tayca) while N-doped TKP 102 was the less active photocatalyst due to N impurities on the TiO_2 acting recombination centres. Chiou et al. [62] studied the effect of Pr^{3+} dopant concentration (0.018-0.22mol%) on the photocatalytic degradation of phenol. Using the undoped sample, 42% of 50mg/l phenol was degraded after 2h irradiation. The degradation efficiency increases with increasing Pr concentration. The highest degradation is observed to be 94.4% with the sample containing 0.072mol% Pr^{3+} that was annealed at 600^oC. A further increase in Pr concentration to 0.22mol% leads to a slight decrease of degradation efficiency to 91.3%. In the Pr-doped TiO_2 particles, Pr^{+3} works as an electron scavenger; this may react with superoxide species and prevent the hole-electron recombinations, and thus increase photooxidation efficiency. However, the degradation was lower than 80% with undoped and other metal-doped TiO_2

particles under similar conditions. Zaleska et al. [114] studied 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 photoactivity of the obtained $B-TiO_2$ than pure TiO_2 under UV light. All tested TiO_2 powders with boric acid series have almost the same photoactivity under visible light. Naeem et al. [105] 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 of 8-11nm. The highest degradation efficiency was found at 0.5mol% Fe^{3+}-doped TiO_2. Liqiang et al. [89] tested the efficacy of La-doped TiO_2 prepared by sol-gel method for the photocatalytic degradation of phenol. After 2 hour calcination at 600^oC, the order of photocatalytic activity of La-doped TiO_2 for phenol degradation was demonstrated to be 1> 1.5> 3> 0.5> 5>0 mol% La. This is related to the La dopant which could inhibit the crystallite growth and the phase transformation of TiO_2 nanoparticles so that the surface content of oxygen vacancies or defects increased. Venkatachalam et al. [53] reported that, under identical and optimal experimental conditions, 1mol% Mg^{2+} and Ba^{2+} doped nano TiO_2, Nano TiO_2 and P-25 required 300, 360 and 450 min respectively for complete mineralisation of 4-Chlorophenol. The photocatalytic degradation of 4-CP over TiO_2 and Mg^{2+} and Ba^{2+} doped TiO_2 indicated the higher activity for doped TiO_2 . Enhanced adsorption of 4-CP on the catalyst surface and smaller particle size due to Mg^{2+} and Ba^{2+} loadings are indicated to be the cause for higher activity of the catalysts.

Lee et al. [115] studied the photocatalytic activity of carbon-doped TiO_2 powders synthesized by the sol-gel method for the degradation of phenol under visible light (λ>420nm) irradiation. The particles contain a certain fraction of oxygen vacancies in the anatase structure as evidenced by XPS results. Under the conditions tested, carbon doped TiO_2 was reported to be efficient for the degradation of phenol. The high photocatalytic activity of C-doped TiO_2 was attributed to the band gap narrowing effect by vacancy states in the anatase structure stabilized by carbon doping. Doping shifted the absorption edge to a lower energy level, thus effectively increasing the photocatalytic activity in the visible-light region. Tian et al. [104] studied the photocatalytic activity of V-doped TiO_2 for the degradation of MB and 2,4-dichlorophenol using UV and visible light. In the presence of UV light, 0.5% $V-TiO_2$ was reported to be efficient for the degradation of MB relative to pure TiO_2. Under visible light irradiation, the degradation rate of 2,4-dichlorophenol over 1% $V-TiO_2$ is shown to be two times higher compared to undoped TiO_2. Yuan et al. [73] studied the influence of co-doping of Zn^{2+} and Fe^{3+} on the photocatalytic degradation of phenol under solar light irradiation. The co-doping of 0.5mol% Zn^{2+} and 1mol % Fe^{3+} onto TiO_2 was found to be two times more efficient compared to pure TiO_2. This behaviour was attributed to the coupled influence of the co-dopant and titania energy bands. Lee et al. [116] compared the photocatalytic degradation of p-nitrophenol over TiO_2 and TiO_2/SiO_2 nanoparticles prepared by the micro-emulsion method using PFPE-NH_4 surfactant. TiO_2/SiO_2 (80:20) nanoparticles were reported to have a higher photocatalytic activity than pure TiO_2 and the TiO_2/SiO_2 (90:10) particles. This effect has been attributed to the decrease in crystallite

size from 17 to 13 nm with an increase in silica content. Under the conditions tested, Silva et al. [103] noticed an optimum Ce content of 0.6% (w/w) into the TiO_2 matrix for enhanced degradation of 4-chlorophenol in the visible light. In addition to the retardation of phase transformation, this behaviour was related to the shift of TiO_2 absorption edge towards longer wavelengths, by reducing the band gap of the original material.

Wang et al. [117] compared the photocatalytic degradation of phenol in the presence of N_2-doped TiO_2 and P25 under visible and sunlight irradiation. The photocatalytic activity of the N_2-doped TiO_2 with anatase phase is shown to be higher than that of the P25 under visible light irradiation. P25 exhibits higher photoactivity for the degradation of phenol compared to N_2 doped TiO_2. Kim et al. [118] 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. TEM and EDS analysis indicated that the added Ni atoms were distributed in the rutile TiO_2 lattice which had an average grain size of 2-4nm. BET analysis showed that Ni-doped powder has a larger surface area ($234m^2/g$) than the other powders (100-$150m^2/g$).The UV/VIS-DRS absorption showed that the nano-sized Ni-doped powder had a higher wavelength range (480-500nm) than the anatase and rutile powder (380-500nm). Under both UV and visible light irradiation, the effectiveness of Ni 8 wt%-doped TiO_2 (234) for the photocatalytic degradation of 4-CP was much higher than that of other powders (100-$150m^2/g$). Adan et al. [102] investigated the effect of Fe^{3+} doping (0.4-5.1wt%) on the photocatalytic degradation of phenol. The photocatalytic activity is shown to be enhanced upon doping with Fe^{3+} up to ca.1wt%. Doping above ca.3wt% does not produce any enhancement of the catalytic activity. Nahar et al. [119] examined the dependence of the photocatalytic degradation of phenol on Fe content under UV and visible light irradiation. An increase in the Fe^{3+} content (Fe/Ti, x =0.002 to 0.005) is reported to increase the photocatalytic activity, however, the overloaded Fe (x=0.008, 0.01) considerably decreased the rate, even below the undoped TiO_2. This effect was ascribed to the balance of excited electron/hole trapped by the doped Fe^{3+} and their charges recombination on the doped Fe^{3+} level. The molar ratio of Fe/Ti (x=0.005) was optimum for both the UV and solar light irradiations. The UV activity was 4.3 times higher than that of the visible light activity. Gorska et al. [120] compared the efficiency of phenol degradation for N, C doped-TiO_2 prepared by TIP hydrolysis under visible light to P-25 irradiated by UV light. In the Vis/N,C-TiO_2 and UV/P-25 systems, nearly 60 min irradiation resulted in 69 and 76% of phenol degradation respectively. However, photocatalytic activity under visible light (> 400nm) of N,C-TiO_2 was four times higher than photoactivity of P-25 TiO_2. Phenol degradation efficiency for commercial TiO_2/UV and doped TiO_2/Vis systems was reported to be comparable.

4. CONCLUSION

Based on recent representative investigations, the role of various operating parameters on the photocatalytic degradation of various phenols and substituted phenols has been explored in this review. TiO_2 has been suggested to be efficient for the degradation and mineralisation of various toxic organic

pollutants such as phenols and dyes in wastewater water in the presence of UV, visible or solar light and oxygen. The findings also suggest that various operating parameters such as photocatalyst type, light intensity, pollutant type 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 influence significantly the photocatalytic degradation rate of phenols. Optimising the degradation parameters is crucial from the perspective of efficient design and the application of photocatalytic oxidation processes to ensure sustainable operation. The application of this technique on actual mixed matrices merits further investigation to yield stable pollutant removal through the optimisation of process parameters. Metal and non-metal doped TiO_2 have been reported to result in improved degradation rates. While doped TiO_2 has shown significant improvement in the efficiency of TiO_2 to remediate wastewater in laboratory scale systems, it is evident that the need to develop pilot scale treatment systems and to apply the technique in cost effective wastewater purification processes requires continued in-depth research. In spite of extensive investigations, the commercial exploitation of photocatalysis has been hindered by the lack of efficient and low cost visible light harvesting catalysts, a relatively poor understanding of reactor design criteria, and inadequate scale up strategies. Future research should focus on the development of a more reliable photocatalyst that can be activated by visible and solar light or both. In addition, more work is required on the modelling of the photoreactor to optimise its design for pollutant degradation. In the literature, there is currently little information on this aspect. Present research activities at CQ University and QUT, Australia focus on the computational fluid dynamics modelling of a flat plate reactor to optimise its design and to predict its performance. Although this review is not comprehensive in the scope of the photocatalytic degradation of organic pollutants, it does however address the fundamental principles and recent applications in this area.

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