

## CHAPTER II

### BACKGROUND AND LITERATURE SURVEY

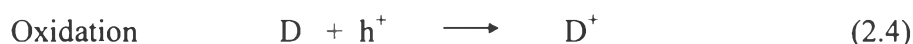
#### 2.1 Principle of Photocatalysis Reaction

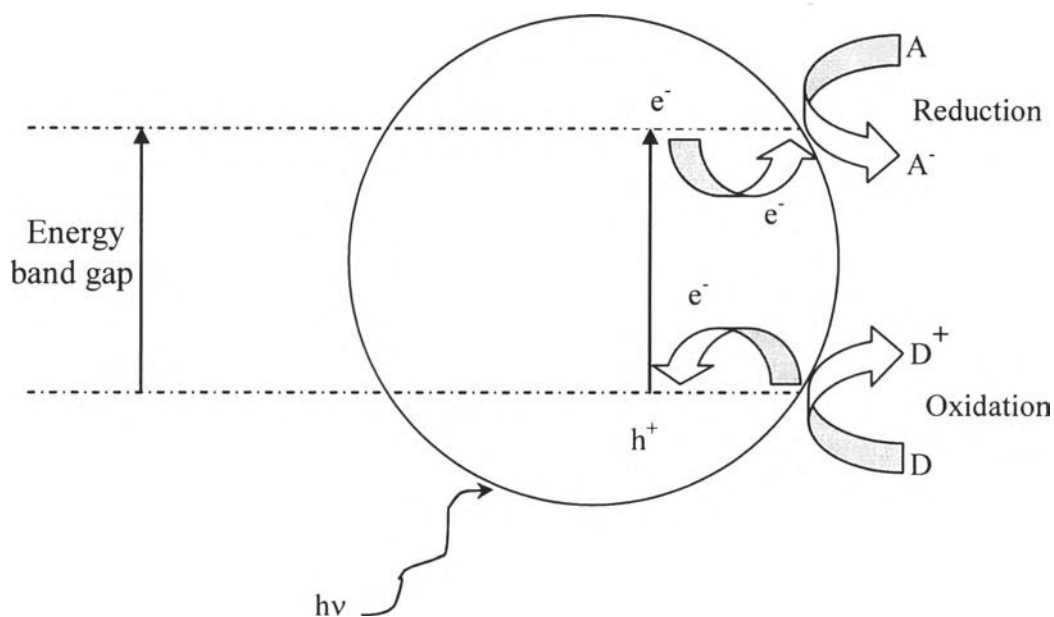
Photocatalysis involves photochemistry and catalysis. Heterogeneous photocatalysis, of which reactant and catalyst are initially in separate phase, consists of light and solid catalyst used together to minimize organic pollutant (Herrmann, 1999). In this process, an organic pollutant completely transforms to CO<sub>2</sub>, H<sub>2</sub> and mineral acids with mechanism as shown in Equation (2.1). Organic compounds containing phosphorus, sulfur and halogen heteroatom may be oxidized quantitatively yielding phosphate (PO<sub>4</sub><sup>3-</sup>), sulfate (SO<sub>4</sub><sup>2-</sup>) and halide (X<sup>-</sup>), respectively (Choi and Hoffmann, 1995). The difference between conventional catalysis and photocatalysis is the mode of activation of the catalyst, in which the thermal activation is replaced by a photonic activation (Herrmann, 1999).



A semiconductor (SC) is characterized by electronic band structures that are occupied valence band (vb) and unoccupied conductance band (cb). These two bands are separated by a band gap. Photocatalysis occurs when a catalyst, which normally is a semiconductor such as TiO<sub>2</sub>, is illuminated with light that has energy higher or equal to the band gap. Then, an electron from the vb is promoted to the cb with simultaneous generation of a hole (h<sup>+</sup>) in vb as illustrated in Figure 2.1.

The possible reaction mechanism of photocatalysis after illuminating with light at an appropriate wavelength shown below (Robertson, 1996).





**Figure 2.1** Mechanism of photocatalytic process of a semiconductor (Litter, 1999).

Generated electron ( $e^-$ ) and hole ( $h^+$ ) can recombine either directly or indirectly by radiative and nonradiative processes on surface or in the bulk of catalyst particles in a few nanoseconds with generating heat or light or can react with donor (D) or acceptor (A) species, which adsorb or close to the catalyst surface. The donor species reacts with hole at vb by oxidation reaction, but the acceptor species receives electron at cb by reduction reaction.

The oxidation reaction is more important in photocatalytic degradation because it is the main reaction for organic pollutant degradation. There are two possible mechanisms, which are direct hole oxidation and hydroxyl radical ( $OH^\bullet$ ) oxidation (Ilisz and Dombi, 1999). For the direct hole oxidation, the photohole reacts directly with the adsorbed organic molecules as shown in Equation (3.3) while, for the  $OH^\bullet$  oxidation, the photohole reacts with surface hydroxyl group ( $OH$ ) or adsorbed water and hydroxyl radical ( $OH^\bullet$ ) will be formed. This hydroxyl radical has high oxidation potential, so normally  $OH^\bullet$  oxidation tends to be the main mechanism in the photocatalytic oxidation. It can react rapidly and non-selectively with most organic compounds and convert them into carbon dioxide, water and other

inorganic compounds (De Lasa *et al.*, 1992). The  $\text{OH}^\bullet$  oxidation reactions are the followings.



The recombination between electron and hole must be avoided because it inhibits the oxidation reaction. Adding some electron scavengers such as oxygen molecules will delay the recombination since they can trap electrons out from the positive hole and transform into superoxide radical ion ( $\text{O}_2^{\bullet-}$ ) and lead to the additional formation of hydroxyl radical (Litter, 1999). Furthermore, as reported by De Lasa *et al.* (1992), it has been pointed out that both  $\text{H}_2\text{O}$  and  $\text{O}_2$  are essential species in the photocatalytic process.



## 2.2 Photocatalyst

A semiconductor used as a photocatalyst should be an oxide or sulfide of metals such as  $\text{TiO}_2$ ,  $\text{CdS}$ ,  $\text{ZnO}$  because electron of metal in vb can move to cb by appropriated energy, which is higher or equal to the band gap (Robertson, 1996). The common properties of several semiconductor show in Table 2.1.

$\text{TiO}_2$  is a popular photocatalyst because the band gap is considerably high around 3.0 eV. It can be activated in the near ultraviolet light (~380 nm). Other types of semiconductors that can be used as a photocatalyst such as  $\text{ZnO}$  or  $\text{CdS}$  may not be applicable due to a toxic  $\text{Zn}^{2+}$  is found (De Lasa *et al.*, 1992).  $\text{CdS}$  also has the toxicity problem due to  $\text{CdS}$  photocorrosion (Reutergardh and Iangphasuk, 1997).  $\text{TiO}_2$  is more stable and insoluble in aqueous solution than  $\text{ZnO}$  and  $\text{CdS}$ . It has been

shown that TiO<sub>2</sub> does not lose its activity when reused (De Lasa *et al.*, 1992). Apart from highly corrosive resistance, TiO<sub>2</sub> is considerably inexpensive.

There are three crystalline forms of titania in nature: anatase, rutile, and brookite. Anatase is the preferred form used as a catalyst and catalyst support. Furthermore, anatase typically has a higher surface area than rutile and observed to be active and stable over long irradiation time (Cheng *et al.*, 1995).

**Table 2.1** Band positions of some common semiconductor photocatalysts (Robertson, 1996)

Semiconductor	Valence band (eV)	Conductance band (eV)	Band gap (eV)	Band gap Wavelength (nm)
TiO <sub>2</sub>	+3.1	+0.1	3.1	380
SnO <sub>2</sub>	+4.1	+0.3	3.9	318
ZnO	+3.0	-0.2	3.2	390
ZnS	+1.4	-2.3	3.7	336
WO <sub>3</sub>	+3.0	+0.2	2.8	443
CdS	+2.1	-0.4	2.5	497
CdSe	+1.6	-0.1	1.7	730
GaAs	+1.0	-0.4	1.4	887
GaP	+1.3	-1.0	2.3	540

### 2.3 Metal-Loaded TiO<sub>2</sub>

Several attempts have been made to improve the activity of pure TiO<sub>2</sub> by doping several kinds of metal, but it has shown both positive and negative effects. So, many works try to find the optimum metal doping to increase stability and the catalytic activity.

Brezova *et al.* (1997) studied the phenol decomposition using different metal-loaded TiO<sub>2</sub> photocatalysts prepared on glass fibers by the sol-gel method. The metals used in this study were Li<sup>+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Ce<sup>3+</sup>, Cr<sup>3+</sup>, Co<sup>3+</sup>, Fe<sup>3+</sup>, Al<sup>3+</sup>, Mn<sup>2+</sup> and Pt<sup>0</sup> and all metals were loaded at 5 mol% metal/TiO<sub>2</sub>. The presence of metals

such as  $\text{Li}^+$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pt}^0$  improved the photoactivity of the  $\text{TiO}_2$  layer prepared on glass fibers by the sol-gel technique. On the other hand, the presence of  $\text{Ce}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Co}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$  and  $\text{Mn}^{2+}$  in the  $\text{TiO}_2$  layer supported on glass fibers has a detrimental effect on the photoactivity of phenol decomposition. The deleterious effect was explained by the fact that trivalent and pentavalent ions behave as recombination centers of the photoproduced charge carriers.

Blazkova *et al.* (1998) studied the photocatalytic decomposition of phenol on sol-gel immobilized  $\text{TiO}_2$  with varying %Pt loading. The Pt loading was varied from 0.5-5.0 mol%  $\text{Pt}^0:\text{Ti}^{4+}$ . The best result was obtained for Pt/ $\text{TiO}_2$  with 1.25 mol% Pt. For the concentration of Pt  $\geq 5$  mol%, it was found to have a pernicious effect on the photocatalyst activity. The major role of Pt on  $\text{TiO}_2$  is to accelerate the superoxide radical anion  $\text{O}_2^{\bullet-}$  formation and consequently decrease the recombination. The increasing of Pt loading to a certain level causes the electron transfer of photoelectron from the semiconductor to the metal particles, decrease of  $\text{O}_2^{\bullet-}$ , resulting in the increase of recombination and decrease of the photocatalytic activity for phenol decomposition.

Phuaphromyod (1999) studied the photocatalytic degradation of isopropyl alcohol using Pt,  $\text{TiO}_2$ , and Pt/ $\text{TiO}_2$ . Pt or  $\text{TiO}_2$  alone showed a low activity but Pt/ $\text{TiO}_2$  had a much higher activity for the degradation of isopropyl alcohol.

Tharathonpisutthikul (2000) studied the photocatalytic degradation of 4-CP by using  $\text{TiO}_2$ , Pt/ $\text{TiO}_2$ ,  $\text{TiO}_2\text{-SiO}_2$  and Pt/ $\text{TiO}_2\text{-SiO}_2$  prepared by the sol-gel method. It was found that the addition of a small amount of Pt into  $\text{TiO}_2$  improved the catalyst activity and the highest activity was obtained with 1% Pt/ $\text{TiO}_2$ . For  $\text{TiO}_2\text{-SiO}_2$  catalyst, the highest activity was achieved at 10%  $\text{SiO}_2\text{-TiO}_2$  because of its highest adsorption capacity. For Pt/ $\text{TiO}_2\text{-SiO}_2$  with 1% Pt and 10%  $\text{SiO}_2$ , although 1% Pt or 10%  $\text{SiO}_2$  alone in  $\text{TiO}_2$  could improve the catalytic activity, the synergistic effect of adding both 1% Pt and 10% Si was not observed due to the agglomeration of the catalyst, which, in turn, lowered the catalytic activity.

Moonsiri *et al.* (2004) studied the effect of Ag/sol-gel  $\text{TiO}_2$  on the degradation of 4-CP. A series of Ag/sol-gel  $\text{TiO}_2$  were prepared at different Ag loadings from 0.2-1.5 mol%. 0.5 mM 4-CP and 0.5 g/l catalyst were used. It was

found that the presence of Ag did not significantly affect the degradation of 4-CP but had the effect on the intermediate products and TOC degradation and 0.5 mol% Ag/sol-gel TiO<sub>2</sub> had a minimum value of TOC at 360 min. With a Ag content greater than 0.5 mol%, the TOC removal increased with increasing Ag loading. It was suggested that a small amount of Ag on TiO<sub>2</sub> attributes to the acceleration of superoxide radical anion, O<sub>2</sub><sup>•-</sup>, formation resulting in decreasing the recombination process while enhances the photoactivity.

Wongvisate (2003) studied the effect of Ag and/or Au doping sol-gel TiO<sub>2</sub>. Au/TiO<sub>2</sub>, Ag/TiO<sub>2</sub> and Au-Ag/TiO<sub>2</sub> were prepared by the sol-gel method with 0.05-1.5 wt% metal doping. The catalytic activity was tested in a batch reactor with the suspension of the catalyst in the solution under UV-C illumination. The result showed that the presence of Au did not significantly improve the photocatalytic efficiency (TOC degradation), but 0.1%Ag/TiO<sub>2</sub> and 1%Au-1%Ag/TiO<sub>2</sub> did.

## 2.4 Immobilization

Many laboratory scale photocatalysis reactors carried out through batch operation and suspension of fine catalyst particles. Consequently, the catalyst separation, expensive and inconvenience, is needed. As a result, immobilization of a catalyst on a support is more attractive. Immobilization is the process that adheres fine particles of a catalyst on a support, which is quartz, glass, stainless steel etc., by different methods (shown in Table 2.2). The TiO<sub>2</sub>/quartz gave the highest photocatalytic activity than glass and stainless steel. In addition, TiO<sub>2</sub>/glass and TiO<sub>2</sub>/stainless steel showed the same activity that was much higher than photolysis (Fernández *et al.*, 1995). Immobilization techniques used included dip coating, sol-gel related methods, electrophoretic and spray coating. After that, annealing with proper temperature and time for improving adhesion and preventing detaching of catalyst was followed. During annealing, Na<sup>+</sup> and Si<sup>4+</sup> from stainless steel and Fe<sup>3+</sup> and Cr<sup>3+</sup> from stainless steel diffuse and dissolve in lattice of titania constitute electron-hole recombination centers. Hence, it decreases activity but quartz is still stable under heating (Fernández *et al.*, 1995).

Byrne *et al.* (1998) studied photocatalytic activity with two different methods, electrophoretic and spray coating, to immobilize TiO<sub>2</sub> on stainless steel. The first method had higher activity than the other. In addition, the equipment required for electrophoretic coating is inexpensive compared to spray pyrolysis technology, which uses a high vacuum reactor. Optimum temperature for annealing of TiO<sub>2</sub>/stainless steel was 775 K. Optimum voltage, which dictated thickness of TiO<sub>2</sub> layer, was 50 volt. Comparison between Ti, Ti-alloy, tin oxide coated glass and stainless steel showed that stainless steel had the highest photocatalytic activity.

Koichi *et al.* (1998) investigated a number of sol-coating, which related to an amount of TiO<sub>2</sub>, on decomposition of oxalic acid. This experiment was carried out in a tubular continuous-flow photoreactor packed with TiO<sub>2</sub> immobilized on gel beads, which are transparent. The optimum number of sol-coating was one. The increasing of the coating numbers resulted in decreasing photocatalytic activity. In one coating, TiO<sub>2</sub> was deposited like film, while repeated sol-coating deposited TiO<sub>2</sub> appeared as a small rectangular pieces, which was a cracked film. Decreasing activity may be due to the decrease in light intensity by increasing the thickness of TiO<sub>2</sub> layer.

Arabazis *et al.* (2002) examined the catalytic activity of TiO<sub>2</sub> (Degussa P25) powder, TiO<sub>2</sub> (Degussa P25) film and Ag/TiO<sub>2</sub> (Degussa P25) film on methyl orange (MO) degradation. Silver-ion (Ag<sup>+</sup>) was deposited on TiO<sub>2</sub> film by dipping in the AgNO<sub>3</sub> solution. The optimum AgNO<sub>3</sub> for the MO degradation was 10<sup>-3</sup> M. A further increase in the Ag<sup>+</sup> concentration resulted in decreasing the efficiency due to a shading of illuminated surface area by silver layer. The silver-modified thin film showed well reproducibility even after six consecutive experiments, and its activity was more efficient compared to the pure TiO<sub>2</sub> film. Unfortunately, the efficiency of the silver-modified film was lower than the slurry-type reaction. It can be explained that on the titania film sample, the active site was hidden by its layer and support surface.

Strength of thin film is an important parameter on photocatalysis in order to increase the life time of catalytic activity. Shibata *et al.* (2003) studied the improvement of a thin film immobilized on a glass substrate of titania. The film composed SiO<sub>2</sub> improved the titania thin film strength remarkably. Unfortunately,

the addition of the silica binder was found to decrease the photocatalytic activity. So, the removal of silica on film surface by immersing in NaOH solution gave a higher photocatalytic activity.

## 2.5 Photocatalytic Reactors

### 2.5.1 Type of Photocatalytic Reactors

Based on the arrangement of light source and reactor vessel, two types of photocatalytic reactors are immersion type with lamp(s) immersed in liquid within the reactor and external type. An external type reactor is a distributive type. The light of this reactor distributes from the source, which is present outside the reactor, to the reactor by optical means.

Ray (1999) studied the performance of a multi-tubular reactor, which is a distributed type fixed-bed reactor. This reactor used hollow glass tubes as light conductors and coat catalyst on outside of the hollow glass tubes. As a result, the reactor can deliver light without loss to liquid. This reactor has higher illumination on the catalyst surface than classical annular reactor (CAR) and tube light reactor (TLR) with catalyst immobilized on glass of light source but the activity is still lower than the slurry reactor (SR). However, multiple tube reactor (MTR) has higher efficiency than SR and CAR but still lower than TLR because of uninformed distribution along the tube (Ray and Beenackers, 1998).

Koichi *et al.* (1998) used the tubular continuous-flow photoreactor consisting of a Pyrex glass tube 8 mm in diameter packed with TiO<sub>2</sub> immobilized on 2 mm diameter gel beads to decompose oxalic acid in excess water under irradiation using fluorescent lamps. High flowrate of oxalic solution gave high efficiency of oxalic decomposition. The problem with this reactor is high resistant to solution flow due to dense packing of small granular silica gel particles.

Chen *et al.* (2001) introduced a new reactor with TiO<sub>2</sub> immobilized on novel supports of Pyrex glass springs. The dimension of the spring packing are : free height (L) = 20.00 mm, span (l) = 0.70 mm, outer diameter (D) = 4.60 mm and wire diameter (d) = 0.75 mm. The advantages of this spring packing are no mass transfer



limitation, low pressure drop, uniform light distribution throughout the bed, large  $\kappa$  value even when the packed depth increased.

**Table 2.2** Method of immobilization of TiO<sub>2</sub> and support substrates (Byrne *et al.*, 1998; Chen *et al.*, 2001)

Method of immobilization	Substrates
Dip coating from suspension	Glass beads, Glass tubing, Glass plate, Glass fibres, Tin oxide coated glass, Silica gel, Sand Pyrex glass bead
Sol gel related methods	Quartz, Optical fibres, Glass beads, Silica gel, Glass plate, Tin oxide coated glass, N/A(formation of stable gel)
Oxidation of parent metal	Titanium
-Electrochemical	
-Thermal	Titanium, Titanium alloy
Anodisation of TiCl <sub>3</sub>	Tin oxide coated glass, Ti, Pt, and Au
Electrophoretic coating	Stainless steel
Plasma spray	Titanium alloy
Aerosol powder coating	Hollow glass beads
Sputtering	Quartz
Liquid phase deposition	Glass plate

Nakashima *et al.* (2002) investigated the degradation of 17 $\beta$ -estradiol (E2), bisphenol-A (BPA), and 2,4-dichlorophenol in aqueous solutions using TiO<sub>2</sub> immobilized on polytetrafluoroethylene (PTFE) mesh sheets and black-light fluorescent lamps. Two reactors with different configuration were used in this study. For the first type, the TiO<sub>2</sub>-modified PTFE mesh sheets were arranged horizontally at 5 mm interval along the reactor in which the solution was circulated at 340 ml/min horizontally. The other reactor used the TiO<sub>2</sub>-modified PTFE mesh sheets attached to a bar-rotator which was rotated at 60 rpm. The latter technique with 0.050 min<sup>-1</sup> first-

order rate constant showed the higher effective and efficient procedures than the former with  $0.033 \text{ min}^{-1}$  first-order rate constant because of higher mass transfer rate. Interestingly, the  $\text{TiO}_2$ -modified PTFE mesh sheet could be re-used under UV-illumination with the same reaction rate.

### 2.5.2 Design of Photocatalytic Reactor

The important parameters for design a photocatalytic reactor are light distribution inside the reactor through absorbing and scattering liquid to the catalyst and surface area of catalyst immobilizing on support per unit volume of reactor. The volume of photocatalytic reactor for well mixing is expressed as (Ray, 1999)

$$V_R = \frac{QC_{in}X}{\eta\kappa\mathfrak{R}} \quad (2.12)$$

where  $Q$  is the volumetric flowrate ( $\text{m}^3/\text{s}$ ),  $C_{in}$  is the inlet pollutant concentration ( $\text{mol}/\text{m}^3$ ),  $X$  is the fractional conversion desired,  $\eta$  is the effectiveness factor (the ratio of actual rate to observed rate),  $\kappa$  is illuminated catalyst surface area in contact with reaction liquid inside the reactor volume ( $\text{m}^2/\text{m}^3$ ) and  $\mathfrak{R}$  is the average mass destruction rate ( $\text{mol}/\text{m}^2 \cdot \text{s}$ ).

Hence, the volume of reactor can be minimized by maximizing  $\mathfrak{R}$  and  $\kappa$  at specific values of  $Q$ ,  $C_{in}$ , and  $X$  in the same condition.  $\mathfrak{R}$  expresses the performance of catalyst for breakdown of a specific model component. To increase  $\mathfrak{R}$ , some modification of a catalyst such as structure and morphology or by addition of additional oxidizing agents can be done.  $\kappa$  represents the amount of a catalyst that is sufficiently illuminated inside the reactor. Thus, that means the catalyst is active and in contact with reaction liquid.

## 2.6 Parameters Influencing the Photocatalytic Rate of Organic Degradation

### 2.6.1 Light Source

Stafford *et al.* (1997) investigated the effect of light wavelength on the rate of photocatalytic degradation of 4-CP. In this experiment, two lamps, a 450

W medium pressure mercury lamp ( $\lambda > 340$  nm) and an 8 W black light lamp ( $\lambda_{\text{max}} = 350$  nm), were used. Other parameters were kept constant. With the 8 W black light lamp, the rates were slower and the maximum concentration of intermediates was lower because of the lower light intensity. It was reported that when a lamp with lower intensity was used, subsequent reactions of intermediates occurred at relatively faster rates than that of the degradation of 4-CP. Therefore, the rate of mineralization was more rapid. This enhancement rate of mineralization at the lower light intensity may occur because the slower rate of hole production allows the other species in solution to come into adsorption equilibrium with  $\text{TiO}_2$ . The other reason is that when the lower wavelength is used, electrons adsorb more energetic photons and the higher energy electrons are less likely to recombine. Therefore, the photoactivity increases with decreasing light wavelength.

Blazkova *et al.* (1998) studied the effect of light sources on the phenol degradation using Pt/ $\text{TiO}_2$  immobilized on glass fibers. Four standard emission lamps were used as the irradiation sources, maximum intensity at 320, 350, 410 nm and white lamp resembling the solar spectrum. The highest photoactivity was obtained for the source with maximum intensity at 320 nm. This experimental result was consistent with the result published by Stafford *et al.* (1997). The photocatalytic activity significantly increased with decreasing wavelength. Although the white lamp resembling the solar spectra had lower efficiency, it showed that the prepared Pt/ $\text{TiO}_2$  catalysts may be used for solar applications.

### 2.6.2 Light Intensity

Photocatalytic activity also depends on light intensity on catalytic surface, which contacts with reaction liquid (Koichi *et al.*, 1998). The light intensity decreases with increasing distance between light source and catalyst, turbidity of reaction liquid, etc.

Chen *et al.* (2001) reported that light intensity changed with packing depth in distilled water. The light intensity of spring packing, 0.5% P25 slurry and granular silica gel particles equal zero at 4.00, 0.25, 0.75 cm, respectively. So the spring packing reactor gave highest conversion at 3.00 cm reactor depth.

Nakashima *et al.* (2002) suggested that the degradation of endocrine-disrupting chemical using a low intensity light source took a long time to decompose than in case of a high intensity light source.

### 2.6.3 Initial Concentration

The results from several works showed different trends of the effect of initial concentration on organic degradation. Some of the studies showed that the rate of organic degradation increased with increasing initial concentration. Surprisingly, some studies reported that the rate of degradation decreased with increasing initial concentration. Moreover, some reactions showed that the initial concentration had no significant effect on the process. Freudenhammer *et al.* (1997) found that the rate of dichloroacetic acid on fixed TiO<sub>2</sub> was lower with higher initial concentration of reaction substrate while Theurich *et al.* (1996) showed the rate of 4-CP degradation increased with increasing initial concentration of 4-CP. Besides, Reutergardh *et al.* (1997) found that as the reactive black 5 (RB5) concentration increased, the quantities of intermediates increased as well. For competing through side reactions with the parent dye decomposition, an increase in dye concentration affected the light penetration into the solution. Therefore, at high initial dye concentrations, the optical density in the solution was lower and fewer photons reached the catalyst surface.

Theurich *et al.* (1996) studied the photocatalytic degradation of 4-CP in Degussa P25 suspensions. The concentration of 4-CP was varied from 0.2 to 10 mM. The degradation rate was found to be a function of the initial 4-CP concentration, at least in a certain range, when the other parameters were kept constant. The degradation rate increased with 4-CP concentration and remained constant at 4-CP concentrations greater than 5 mM. One possible explanation for this behavior was that the adsorption of the substrate molecule was the rate limiting. This adsorption was described by the Langmuir-Hinsherwood (L-H) equation,

$$\frac{-d [4-CP]}{dt} = \frac{kK[4-CP]}{1+K[4-CP]} \quad (2.13)$$

where  $d[4-CP]/dt$  is the rate of 4-CP degradation,  $k$  is the reaction rate constant,  $K$  is the adsorption coefficient of 4-CP and  $[4-CP]$  is the concentration of 4-CP. For a

high concentration of the pollutant, where saturation coverage of the TiO<sub>2</sub> surface is achieved ( $K [4\text{-CP}] \gg 1$ ), the L-H equation simplifies to a zero-order rate equation.

$$\frac{-d [4\text{-CP}]}{dt} = k \quad (2.14)$$

For a very low concentration of 4-CP ( $K [4\text{-CP}] \ll 1$ ), the L-H equation changes into a pseudo first-order kinetic law.

$$\frac{-d [4\text{-CP}]}{dt} = k'[4\text{-CP}] \quad (2.15)$$

with  $k' = kK$  being the pseudo first order rate constant. Therefore, at a high initial concentration, the 4-CP degradation obeys the zero order kinetics while the degradation kinetics at the low concentration can be interpreted as an example of the first order kinetics.

#### 2.6.4 Dissolved Oxygen

The presence of oxygen in the photocatalytic systems can significantly affect the fate of the photogenerated species, i.e., it reacts with the conduction band electrons to form superoxide anion radicals, and it combines with organic radicals generated by the hydroxyl radicals attack or by the reaction with photoholes.

Blazkova *et al.* (1998) observed the effect of oxygen flow on the degradation of phenol using Pt/TiO<sub>2</sub> immobilized on glass fibers. It was found that the phenol half-life decreased linearly with increasing the oxygen flow in the photocatalytic degradation of phenol. However, the oxygen flow higher than 5 dm<sup>3</sup>/min under the given conditions damaged the photocatalyst quality.

Phuaphromyod (1999) studied the effect of dissolved oxygen on the photocatalytic degradation of isopropanol. The experiments were carried out by flowing nitrogen, air and oxygen into the isopropanol solution to obtain different levels of dissolved oxygen of 0, 8.8 and 37.7 mg/l, respectively. For the saturated dissolved oxygen of 37.7 mg/l, isopropanol was degraded rapidly and completely within 1.5 hr. The same results were observed with 8.8 mg/l of dissolved oxygen. When nitrogen was bubbled into the solution to obtain zero dissolved oxygen, the

results showed a slight decrease in the isopropanol concentration. It was suggested that the dissolved oxygen had an important role in the photocatalytic degradation of isopropanol since the oxygen molecule can act as an electron trap. The trap separated electrons from the hole and the recombination process was reduced. Hence, the photocatalytic activity increases with increasing the dissolved oxygen. In addition, the oxygen flow served as the stirring medium to enhance the mass transfer rates in the irradiated system.

Moonsiri *et al.* (2004) studied the effect of dissolved oxygen on the 4-CP degradation with 0.5 g/l sol-gel TiO<sub>2</sub>. The solution was aerated with nitrogen while the other experiment was carried out at a very high dissolved oxygen level. It was found that in the presence of oxygen, the degradation rates of 4-CP and TOC were much higher than those of the system without dissolved oxygen. The three intermediate products, hydroquinone, benzoquinone and hydroxyhydroquinone, were generated during the 4-CP degradation without dissolved oxygen but benzoquinone was not generated during the 4-CP degradation in the presence of dissolved oxygen. It can be concluded that the dissolved oxygen not only reduces the intermediate concentrations but also reduces the type of the intermediate products.