CHAPTER II
BACKGROUND AND LITERATURE SURVEY

2.1 Principle of Photocatalysis Reaction

The word "photocatalysis" comes from photochemistry and catalysis. So, the photocatalytic process implies that light and a catalyst are used together to accelerate chemical transformations. 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).

The photocatalytic process involves the utilization of a semiconductor. Most of semiconductors are the oxide or sulfide of metals. When semiconductors are illuminated with light at an appropriate wavelength, they become powerful oxidants, which will convert most organic materials to carbon dioxide, water and inorganic compounds. This process is effective in destroying a wide range of organic materials (Robertson, 1996). The organic compounds containing phosphorus, sulfur and halogen heteroatom may be oxidized quantitatively yielding phosphate (PO_4^{3-}), sulfate (SO_4^{2-}) and halide (X^-), respectively. Nitrogen compounds present the most complex results. The only chlorinated molecule resistant to initial photocatalytic attack is the saturated molecule with no abstractable hydrogen such as carbon tetrachloride. But some studies indicated that the rate of CCl_4 dechlorination could be enhanced significantly when alcohols and organic acids were used as electron donors (Choi and Hoffmann, 1995).

The basic principle of photocatalysis can be described as follows. A semiconductor (SC) is characterized by an electronic band structure that are occupied valence band (vb) and unoccupied conductance band (cb). These two bands are separated by the energy gap called the "band gap" (E_{bg}). When

the semiconductor is illuminated with light that has energy higher or equal to the band gap, an electron from the *vb* is promoted to the *cb* with the simultaneous generation of a hole (h^+) in the *vb* as illustrated in Figure 2.1.
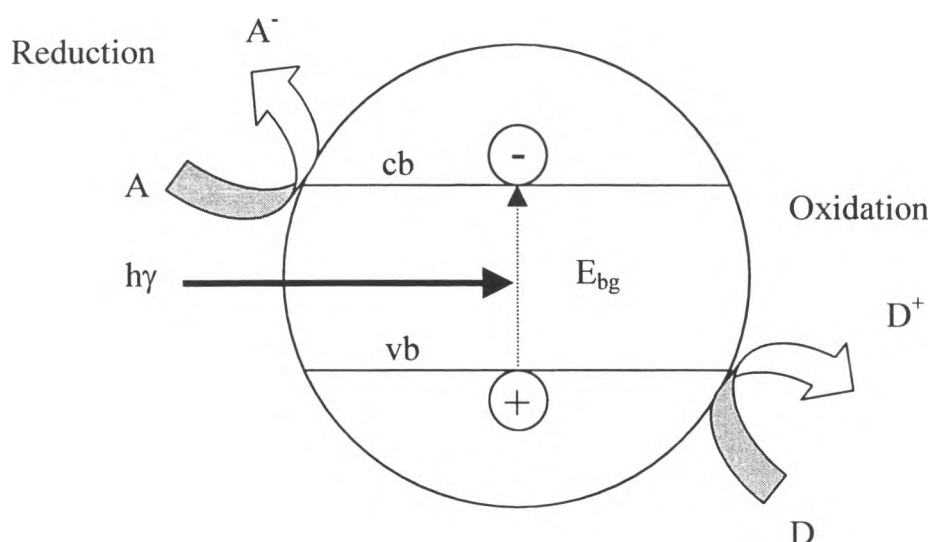

Figure 2.1 Promotion of an electron from the valence band to the conductance band on illumination of a semiconductor (Litter, 1999)

Possible reactions that can occur when a solution containing a semiconductor absorbs a photon (hγ) of a suitable wavelength are shown in the following reactions (Robertson, 1996).

Light absorption	$SC + h\gamma$	$\rightarrow$	$e^- + h^+$	(2.1)
Recombination	$e^- + h^+$	$\rightarrow$	heat	(2.2)
Oxidation	$D + h^+$	$\rightarrow$	D^+	(2.3)
Reduction	$A + e^-$	$\rightarrow$	A^-	(2.4)

The electron and hole pair may recombine on the surface or in the bulk of the particles in a few nanoseconds with the generation of heat or can be trapped in surface state where they can react with other species that are
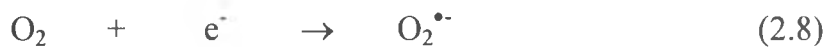
adsorbed or close to the surface of particles. For the example, if an electron donor or species D is adsorbed on the surface, it will react with the hole and the oxidation reaction occurs. On the other hand, if an electron acceptor or species A is adsorbed on the surface, it will receive an electron and the reduction reaction occurs. The energy level at the bottom of the cb is the reduction potential of photoelectron and the energy level at the top of the vb determines the oxidizing ability of photohole. From thermodynamic points of view, adsorbed species can be reduced photocatalytically by cb electrons if they have redox potentials more positive than the flat band of the cb and can be oxidized by vb holes if they have redox potentials more negative than the flat band of the vb (Litter, 1999).

In the photocatalytic oxidation of organic molecules, there are two possible mechanisms when a semiconductor is illuminated with photon energy greater or equal to its band gap energy. Those are direct hole oxidation and $OH^\bullet$ oxidation (Ilisz and Dombi, 1999). Normally, the $OH^\bullet$ oxidation tends to be the main mechanism in the photocatalytic oxidation. For the direct hole oxidation, the photohole reacts directly with the adsorbed organic molecules as shown in equation (2.3) 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. 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 $OH^\bullet$ oxidation reactions are the followings.

$$OH^- \quad + \quad h^+ \quad \rightarrow \quad OH^\bullet \tag{2.5}$$

$$H_2O \quad + \quad h^+ \quad \rightarrow \quad OH^\bullet + H^+ \tag{2.6}$$

$$OH^\bullet \quad + \quad D_{ads} \quad \rightarrow \quad D_{oxid} \tag{2.7}$$

The recombination 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 ($O_2^{\bullet-}$) and lead to the additional formation of hydroxyl radical (Litter, 1999).

$$O_2 \quad + \quad e^- \quad \rightarrow \quad O_2^{\bullet-} \qquad (2.8)$$

$$2H_2O + \quad O_2^{\bullet-} \quad \rightarrow \quad 2H_2O_2 \qquad (2.9)$$

$$H_2O_2 \quad \rightarrow \quad 2OH^{\bullet} \qquad (2.10)$$

It has been pointed out that both H_2O and O_2 are essential species in the photocatalytic process. Photocatalytic oxidation of 4-chlorophenol does not occur in the absence of either H_2O or O_2 or both (De Lasa et al., 1992).

2.2 Types and Forms of Photocatalysts

2.2.1 Types of Semiconductor

A semiconductor used as a photocatalyst should be an oxide or sulfide of metals such as TiO_2, CdS and ZnO. The energy band gap of the photocatalyst should match the energy gained from light sources. The valence band, conductance band, band gap and band gap wavelength of some common semiconductors are shown in Table 2.1.

TiO_2 is a popular photocatalyst because the band gap is around 3.0 eV. It can be activated in the near ultraviolet light (~ 380 nm). Other types of semiconductors that can be used as photocatalysts such as ZnO or CdS may not be applicable due to their toxicity. Moreover, ZnO is corroded by illumination in aqueous solution and toxic Zn^{2+} is found (De Lasa et al., 1992). CdS also has the toxicity problem due to CdS photocorrosion (Reutergardh and Iangphasuk, 1997). TiO_2 is more stable and insoluble in aqueous solution than ZnO and CdS. It has been shown that TiO_2 does not lose activity when reused (De Lasa et al., 1992). Moreover, TiO_2 is corrosion resistant and relatively inexpensive. Therefore, TiO_2 is suitable for the photocatalytic process. Generally, there are three different forms of TiO_2 namely anatase, brookite and rutile. TiO_2 in the anatase form has been

observed to be active and stable over very long irradiation times (Cheng *et al.*, 1995).

Table 2.1 The band positions of some common semiconductor photocatalysts (Robertson,1996)

Semiconductor	Valence band (eV)	Conductance band (eV)	Band gap (eV)	Band gap wavelength (nm)
TiO_2	+3.1	+0.1	3.1	380
SnO_2	+4.1	+0.3	3.9	318
ZnO	+3.0	-0.2	3.2	390
ZnS	+1.4	-2.3	3.7	336
WO_3	+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

2.2.2 Supported TiO_2

Many investigations have been carried out to observe the effect of a variety of supporting materials for the degradation of organic compounds. In general, it is assumed that good supporting materials for TiO_2 as a photocatalyst should have the following attributes: (1) to be transparent to UV radiation, (2) to favor strong surface chemical-physical bonding with the TiO_2 particles without negative affecting their activity, (3) to offer a high specific surface area, (4) to have a good adsorption capability for the organic compounds to be degraded, (5) to be in a physical configuration which favors

the liquid-solid separation, (6) to allow reactor designs that facilitate the mass transfer processes and (7) to be chemically inert (Pozzo *et al.*, 1997).

Catalytic activity of the supported TiO_2 is affected by several factors, for example, the change in the TiO_2 energy band structure because of chemical bond with the support, the alteration of the catalyst crystal structure (determined by the temperature treatment after loading), the decrease of the catalyst surface area is due to catalyst particle agglomeration and catalyst support binding, and catalyst particle trapping inside support pores, where the radiation cannot penetrate (Pozzo *et al.*, 1997).

Torimoto *et al.* (1996) studied the photodecomposition of propyzamide using TiO_2 and TiO_2-loaded adsorbent prepared by the sol-gel method as the photocatalysts. The adsorbent used were zeolite, silica and activated carbon (AC). The adsorption behavior of propyzamide on each photocatalyst was studied. The decreasing order of adsorption capacity is TiO_2/AC, TiO_2/SiO_2, $TiO_2/zeolite$ and TiO_2. For TiO_2/AC, more than 90% of the initial amount of propyzamide was completely converted to CO_2 with irradiation time of 200 minutes, whereas other photocatalysts required longer irradiation time to achieve the same degradation efficiency. The rate of CO_2 production for different photocatalysts were in the following order: $TiO_2/AC >$ $TiO_2/SiO_2 > TiO_2/zeolite > TiO_2$. Besides, this study was shown that using the TiO_2-loaded adsorbents could reduce the concentration of intermediates in the solution phase. It was suggested that the intermediates were adsorbed on the adsorbent/TiO_2 interface and then oxidized further to CO_2 whereas the use of TiO_2 allowed the dissolution of intermediates into solution due to low adsorption ability.

Jung and Park (2000) studied the effect of adding silica into titania prepared by the sol-gel method on the photoactivity of trichloroethylene decomposition. The silica mole fraction was varied from 0.05 to 0.6. The photoactivity of silica/titania was increased by increasing silica content and

reached a maximum at 30 mol% of silica in titania. This highest activity was five times higher than Degussa P25. The added silica helps increasing the thermal stability of titania which, in turn, suppresses the phase transformation of anatase to rutile when the calcination temperature increases. The surface area of silica/titania was increased with increasing the silica content. However, the average pore size and pore volume had the maximum values at 30 mol% of silica. It was suggested that high porosity and large pore size facilitate the mass transfer of reactants and it was responsible for the highest photoactivity at 30 mol% of silica. The enhanced photoactivity of silica/titania was also achieved by simultaneously increasing both the surface area and the crystallinity.

2.2.3 Metal- Loaded TiO_2

Brezova *et al.* (1997) studied the phenol decomposition using different metal-loaded TiO_2 photocatalysts prepared on glass fibers by the sol-gel method. The metal used in this study were Li^+, Zn^{2+}, Cd^{2+}, Ce^{3+}, Cr^{3+}, Co^{3+}, Fe^{3+}, Al^{3+}, Mn^{2+} and Pt^0 and all metals were loaded at 5 mol% metal/TiO_2. The presence of metals such as Li^+, Zn^{2+}, Cd^{2+} and Pt^0 improved the photoactivity of the TiO_2 layer prepared on glass fibers by the sol-gel technique. On the other hand, the presence of Ce^{3+}, Cr^{3+}, Co^{3+}, Fe^{3+}, Al^{3+} and Mn^{2+} in the TiO_2 layer supported on glass fibers has a detrimental effect on the photoactivity of phenol decomposition.

Blazkova *et al.* (1998) studied the photocatalytic decomposition of phenol by varying %Pt loading on TiO_2. The platinum loading was varied from 0.5-5.0 mol% Pt^0: Ti^{4+}. The best results were obtained for the Pt/TiO_2 photocatalyst with 1.25 mol% Pt. For the concentration of Pt $\geq$ 5 mol%, Pt has a detrimental effect on the photocatalyst activity. The major role of platinum on TiO_2 is to accelerate the superoxide radical anion $O_2^{\bullet-}$ formation and consequently decreases the recombination. The increasing of Pt loading to

a certain level causes the electron transfer of photoelectron from the semiconductor to metal particles decrease of $O_2^{\bullet-}$ resulting in the increase of recombination and lowers the photocatalytic activity for phenol decomposition.

2.3 Parameters Influencing the Photocatalytic Rate of Organic Degradation

2.3.1 Light Source

For the photocatalytic process, effect of light intensity can be divided into 3 regions. At low intensity, the degradation rate is first order with respect to light intensity. At intermediate intensity, the reaction rate increases with the square root of intensity. An increase in intensity always increases the reaction rate until the reaction is mass transfer limited. Therefore, at high intensity, the reaction rate is constant due to limitation of mass transfer (De Lasa *et al.*, 1992). Increasing intensity increases the recombination process faster than the oxidation. Even through increasing intensity increases the reaction rate, it lowers the efficiency of the photocatalytic reaction. The regimes of intensity dependence are shown in Figure 2.2.

Stafford *et al.* (1997) studied the effect of light wavelength on the rate of photocatalytic degradation of 4-chlorophenol. In this experiment, two lamps, a 450 W medium pressure mercury lamp ($\lambda > 340$ nm) and an 8 W black light lamp ($\lambda_{max} = 350$ nm), were used. The 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 lamp intensity. It was reported that when a lamp of lower intensity was used, subsequent reactions of intermediates occured at relatively faster rates than that of the degradation of 4-chlorophenol. Therefore, the rate of mineralization was more rapid. This enhanced 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 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.
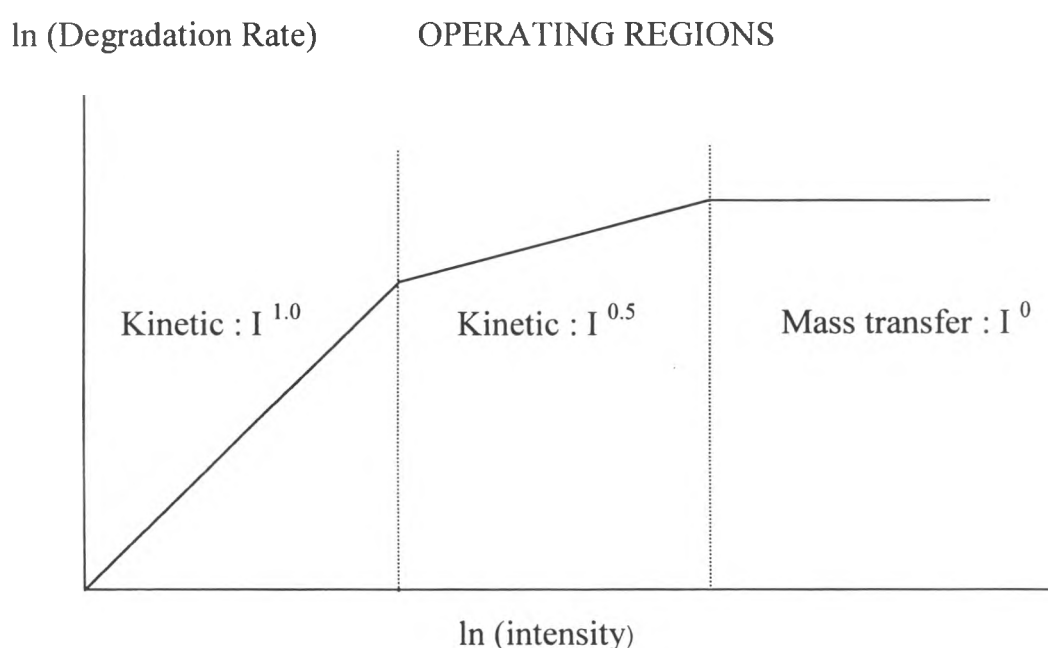
ln (Degradation Rate)   OPERATING REGIONS

Kinetic : $I^{1.0}$ Kinetic : $I^{0.5}$ Mass transfer : I^{0}

ln (intensity)

Figure 2.2 Theoretical regimes for rate dependence on light intensity (De Lasa *et al.*, 1992)

Blazkova *et al.* (1998) studied the effect of light sources on the phenol degradation using Pt/TiO_2 immobilized on glass fibers. The four standard emission lamps were used as the irradiation sources, maximum intensity at 320, 350, 410 nm and white lamp resembling the solar spectrum, respectively. The highest photoactivity was obtained for the source with maximun intensity at 320 nm. This experiment 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 effeciency, it showed that the prepared Pt/TiO_2 catalysts may be used for solar applications.

Herrmann *et al.* (1999) studied the photocatalytic degradation of 4-chlorophenol using the synergistic effect between titania and activated carbon (AC) in aqueous suspension. The light source in this study was solar light. 4-chlorophenol adsorption had been performed at 20 °C on Degussa P25 (50 mg), on activated carbon (10 mg) and on a suspended mixture of them with the same respective masses. The adsorption isotherms were determined assuming a Langmuir isotherm. The amount of 4-chlorophenol adsorbed on TiO_2-AC was slightly smaller than on pure AC. There was no addition of the adsorption capacities of both solids when they were mixed together. The addition of AC to TiO_2 obviously created a kinetic synergistic effect in 4-chlorophenol disappearance, with an increase of the rate constant by a factor of 2.4. The synergistic effect was ascribed to an extended adsorption of 4-chlorophenol on AC followed by a transfer to titania where it was photocatalytically degraded. The beneficial synergistic effect due to the addition of AC to titania also decreased the release of intermediate products in the solution.

2.3.2 Initial Concentration

Theurich *et al.* (1996) studied the photocatalytic degradation of 4-chlorophenol in Degussa P25 suspensions. The concentration of 4-chlorophenol was varied from 0.2 to 10 mM. The degradation process was a function of the initial 4-chlorophenol concentration, at least in a certain range, when other parameters were kept constant. The rate of degadation was the function of 4-chlorophenol concentration increasing up to 5 mM and remaining constant for higher 4-chlorophenol. One possible explanation for this behavior was that the adsorption of substrate molecule was rate limiting.

This adsorption could be described by the Langmuir-Hinsherwood (L-H) equation,

$$-\frac{d[4\text{-}CP]}{dt} = \frac{kK[4\text{-}CP]}{1+K[4\text{-}CP]} \qquad (2.11)$$

where d[4-CP]/dt is the rate of 4-chlorophenol degadation, k is the reaction rate constant, K is the adsorption coefficient of 4-chlorophenol and [4-CP] is the concentration of 4-chlorophenol. For high concentration of the pollutant, where saturation coverage of the TiO_2 surface is achieved (K [4-CP] >>1), the L-H equation simplifies to a zero-order rate equation.

$$-\frac{d[4\text{-}CP]}{dt} = k \qquad (2.12)$$

For very low concentration of 4-chlorophenol (K [4-CP] << 1), the L-H equation changes into a pseudo first-order kinetic law.

$$-\frac{d[4\text{-}CP]}{dt} = k'[4\text{-}CP] \qquad (2.13)$$

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

2.3.3 Amount of Catalyst

Stafford *et al.* (1997) studied the photocatalytic degradation of 4-chlorophenol by varying the amount of TiO_2 in 4-chlorophenol solution. Photocatalytic degradation of 250 μM of 4-chlorophenol was carried out with 0.05 – 1.00 g/l Degussa P25 under UV irradiation. The initial rate of 4-chlorophenol disappearance showed a small increase with increasing TiO_2. At a lower catalyst loading, much of the light was transmitted through the slurry while at a higher catalyst loading, all of photons were adsorbed. The decrease

in the rate of 4-chlorophenol disappearance at the lower loading was explained by the fact that more light was transmitted through the reactor and the transmitted light was not utilized in the reaction. The increase of TiO_2 loading decreased the concentration of intermediates and increased the rate of oxygen consumption. The higher rate of oxygen consumption and lower overall concentration of intermediates indicated that there was more rapid mineralization at the higher TiO_2 loading. But the rate of degradation does not always increase with increasing the amount of catalyst in the slurry photocatalytic processes. The optimum catalyst dosage reported was in the range from 0.15 to 8 g/l for different photocatalytic systems and photoreactors. Even for the same catalyst (Degussa P25), a big difference in optimal catalyst dosage from 0.15-2.5 g/l was reported (Chen and Ray, 1999).

2.3.4 pH of Solution

pH generally influences a semiconductor in an electrochemical system e.g., TiO_2 particles suspended in water because the charge of the semiconductor surface and the adsorption properties depend on the pH. Since in photocatalysis, the adsorption of a pollutant is the first step before its degradation, a change in pH can lead to a change of the degradation rate. The trend of this effect depends directly on the nature of the catalyst and substrate. Moreover, the change in pH can shift the band gap. The valence band decreases by 59 mV for each increasing unit of pH. A higher rate of oxidation should be observed at a lower pH. In the alkaline region, the reaction rate will be enhanced by increasing the hydroxyl ion, OH^- concentration that will transform to the reactive form of hydroxyl radical, $OH^\bullet$ (De Lasa et al., 1992).

Theurich et al. (1996) studied the effect of pH on the photocatalytic degradation of 4-chlorophenol. From this study, the pH of the solution was varied from 3-11. In each experiment, the pH was maintained constantly throughout the irradiation. It was obvious that the 4-chlorophenol

degradation rate was hardly influenced by the pH but a larger amount and higher concentrations of intermediates were found at a higher pH. The number and concentrations of intermediates were reached a maximum at pH 9. The results presented in this study showed that it was very important to select the optimum pH for the photocatalytic degradation process to combine a high efficiency with the suppression of the formation of toxic intermediates.

2.3.5 Dissolved Oxygen

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 the dissolved oxygen 0, 8.8 and 37.7 mg/l, respectively. For saturated dissolved oxygen of 37.7 mg/l, isopropanol was degraded rapidly and completely within 1.5 hours. The same results were observed with 8.8 mg/l of dissolved oxygen. When nitrogen was bubbled into the solution to obtain a zero dissolved oxygen, the results showed a slight decrease of isopropanol concentration. It was suggested that the dissolved oxygen have an important role in the photocatalytic degradation of isopropanol since the oxygen molecule can act as an electron trap. The trap separates electrons from the hole and the recombination process is reduced. Hence, the photocatalytic activity increases with increasing the dissolved oxygen. In addition, the oxygen flow serves as the stirring medium performing the mass transfer in the irradiated system.

Blazkova *et al.* (1998) observed the effect of oxygen flow on the degradation of phenol using Pt/TiO_2 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^3/min under the given conditions damaged the photocatalyst quality.

2.3.6 Temperature

The overall process of photocatalytic degradation is usually not very temperature sensitive. The dependence of degradation rate on temperature is reflected by the low activation energy compared with the ordinary thermal reactions. For example, the activation energy of photocatalytic oxidation of acetone over Pt/TiO_2 was 10-13 kJ/mol while the activation energy of thermal acetone oxidation was 84 kJ/mol (Vorontsov *et al.*, 2000). The influence of temperature is not significant because of the low thermal energy (kT = 0.026 eV at room temperature) that has almost no contribution to the activation of TiO_2 catalyst, which has a high band gap energy (3.2 eV). Therefore, there is no need to heat the system and this absence of heating is very attractive for photocatalytic process carried out in aqueous media, especially for water purification, because there is no need to waste energy in heating water, which has a high heat capacity (Chen and Ray, 1999).