CHAPTER II

THEORY BACKGROUNDS AND LITERATURE REVIEW

2.1 Titanium dioxide (TiO$_2$)

Titanium dioxide (TiO$_2$) is found in nature in three different crystal structures: rutile, anatase and brookite. The two important structures of TiO$_2$, rutile and anatase, are commonly used in photocatalytic purpose. In photocatalysis process, anatase more preferable than rutile due to it provides higher band-gap. Consequently, TiO$_2$ in anatase form has widely application than the rutile form (Augustynski, J., 1993). The structure of rutile and anatase can be described in terms of tetragonal structure, as indicated in Figure 2.1.

Table 2.1 Comparison of rutile and anatase (Linsebigler et al., 1995 and Fujishima et al., 1999)

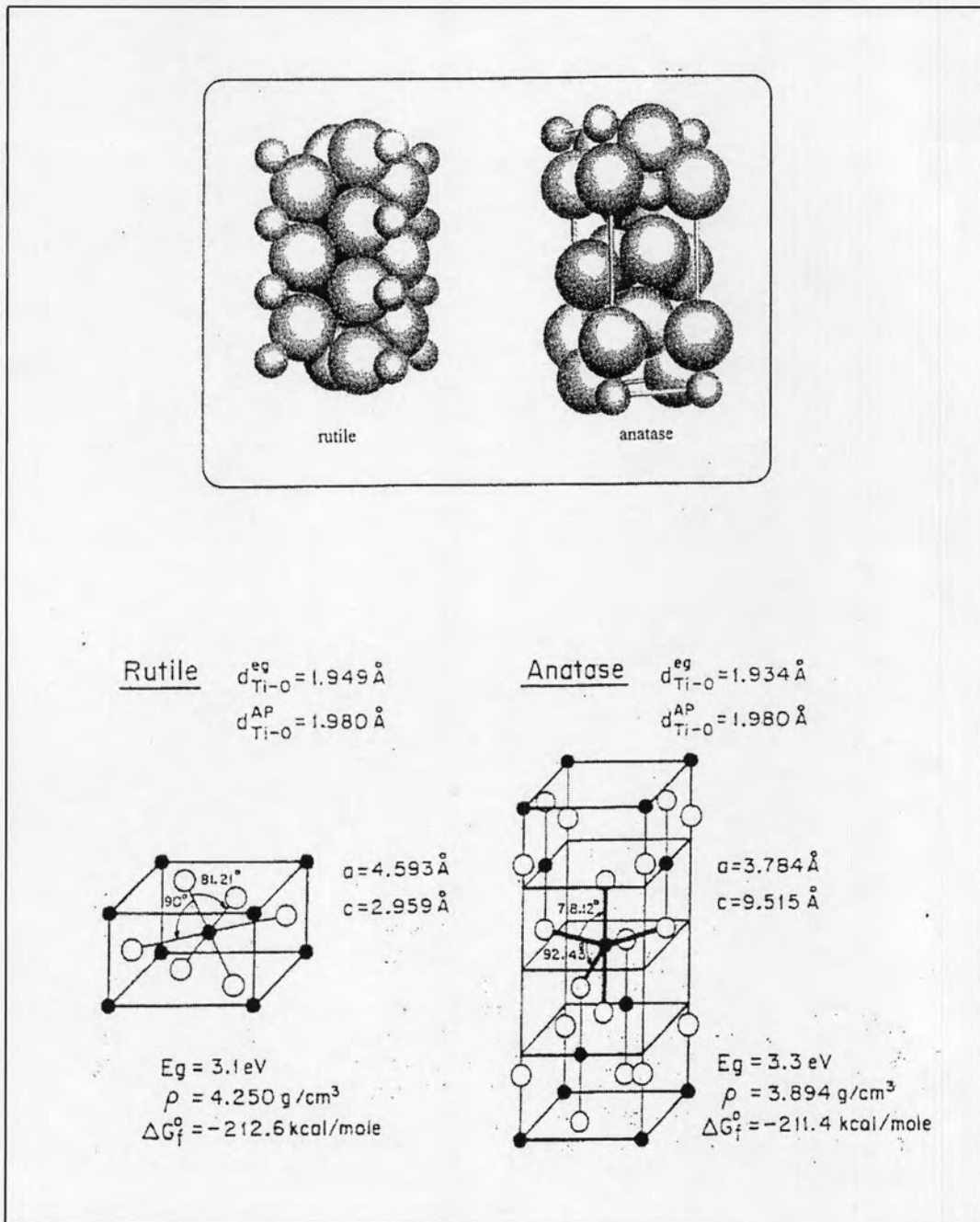| Properties	Rutile	Anatase
Crystalline form	Orthorhombic	Orthorhombic
Band gap energy (eV)	3.030	3.200
Hardness (Mohs)	6.0-7.0	5.5-6.0
Density (g/cm^3)	4.250	3.894
Gibbs free energy, ΔG_f° (kcal/mole)	-212.6	-211.4
Lattice constant, a (A$^\circ$)	4.593	3.784
Lattice constant, c (A$^\circ$)	2.959	9.515
Melting point ($^\circ$C)	1858	Changes to rutile at high temperature 800°C

Figure 2.1 Crystal structure of TiO$_2$: rutile and anatase (Linsebigler et al., 1995; Fujishima et al., 1999)

The anatase polymorph of TiO_2 apparently shows higher photoactivity than rutile. Besides the difference in structure, the energy band structure and surface chemistry are key factors. The band gap energy of anatase is 3.2 eV, which corresponds to UV light (388 nm), while the band gap energy for rutile is 3.0 eV corresponding to violet light (413 nm). The difference in band gap comes from the level of conduction band edge of anatase which is higher than that of rutile by about 0.2 eV. Thus, electrons from the conduction band of anatase have higher reducing power than those of rutile (Fujishima et al., 1999)

The crystal structure of TiO_2 can convert from one to another by using different temperatures. At low temperature, anatase is predominant, whereas if temperature reaches higher than 900°C anatase will transform to rutile. The crystalline phases and particle size of the solid have effect on the catalytic behavior of TiO_2 directly in photocatalysis. Thus, an increase in the anatase particle size seems to be related to an increase in the activity (Kim, D. H. et al., 1994).

Titanium dioxide (TiO_2) in a photocatalytic system is used as a fine powder. The TiO_2 powder is widely used in both laboratory and pilot plant scale in the form of slurry or aqueous suspension. This TiO_2 type offers the advantage of high surface dispersion and, consequently, optimization of the encounter frequency of the active surface of a photocatalyst with a pollutant substrate. (Matthews, 1986; Matthews and McEvoy, 1992; Fujishima et al., 1999)

Recently, most research is focused on modifying the TiO_2 structure to improve TiO_2 properties for various applications. The production of TiO_2 particles with a specific size and morphology is of primary importance for the development of this material. Since the photocatalytic activity for environmental applications is mostly confined to the surface of the photocatalytic material, its surface area must be increased to maximize the photocatalytic activity. One way to do this is the synthesis of nano-sized TiO_2 particles to increase photocatalytic reaction sites on the surface. Also, the amount of the anatase phase must be maximized because the rutile phase shows less photocatalytic activity (Asashi et al., 2001)

In conventional photocatalysis process, TiO_2 is widely used as suspended form. Although it can be used to remove the pollutants efficiently, but it has limitation in adsorption behavior. The limitation can be overcome by immobilizing TiO_2 particles

coat on Activated carbon (AC). Many techniques in synthesizing TiO_2/AC composite, such as chemical vapour deposition (CVD), direct air-hydrolysis (DAH), high temperature impregnation (HTI) (Amjad H. El-Sheikh., 2004) and sol-gel techniques (Dong-Keun Lee., 2004). Among these techniques, sol-gel technique is the most common method of producing TiO_2/AC composite and it is accepted to be the practical process to control the structure of a material on a nanoscale (Dong-Keun Lee., 2004).

2.2 Activated carbon (AC)

Activated carbon (also called activated charcoal) is the more general term which includes carbon material mostly derived from charcoal. It denotes a material which has an exceptionally high surface area, typically determined by nitrogen adsorption, and includes a large amount of microporosity. Sufficient activation for useful applications may come solely from the high surface area, though often further chemical treatment is used to enhance the absorbing properties of the material (Wikipedia, 2007).

The use of special manufacturing techniques results in highly porous charcoals that have surface areas of 300-2000 $m^2 g^{-1}$. There so-called active, or activated, charcoals are widely used to adsorb odorous or colored substances from gases or liquids (howstuffs, 2007)

The macropores provide a passageway to the interior of the particle into the micropores but do not contribute substantially to the particle surface area. The micropores, on the other hand, are responsible for the large surface area of activated carbon particles created during the activation process. It is the micropores where adsorption largely takes place. Thus, two main parameters are relevant to the performance of the activated carbon namely, the surface area and the pore volume or structure. The pore volume limits the size of the molecules that can be adsorbed whilst the surface area limits the amount of material, which can be adsorbed. The mechanical strength of the activated carbon is also an important factor for prevention of damage due to regeneration, recycling etc.

AC uses the physical adsorption process whereby attractive van der waals forces pull the solute out of solution and onto its surface. Once the solute is bound to the carbon is it considered "remove" from the water.

AC adsorption proceeds through 3 basic steps.

1. Substances adsorb to the exterior of the carbon granules.

2. Substances move into the carbon pores.

3. Substances adsorb to the interior walls of the carbon

(The Charles E. Via, 2006)

Principle of Activated Carbon

Activated carbon works by attracting and holding certain chemicals as fluid stream passes through a highly porous material. The contaminant is attracted to and held (adsorbed) on the surface of the carbon particles. The characteristics of the carbon material (particle and pore size, surface area, surface chemistry, density, and hardness) influence the efficiency of adsorption.

Compounds with low water solubility (hydrophobic) are more likely to be adsorbed to a solid. The second criterion is the attraction of the contaminant to the carbon surface. If several compounds are present in the fluid stream, strong adsorbers will attach to the carbon in greater quantity than those with weak adsorbing ability. These combined factors enable the activated carbon material to draw the molecule out of the fluid stream.

Adsorption Characteristics

The adsorption process depends on the following factors:

1) Physical properties of the activated carbon, such as pore size distribution and surface area;

2) The chemical nature of the carbon source, or the amount of oxygen and hydrogen associated with it;

3) Chemical composition and concentration of the contaminant;

4) The temperature and pH of the water; and

5) The flow rate or time exposure of water to activated carbon.

- **Physical Properties**

The amount and distribution of pores play key roles in determining how well contaminants are filtered. The best filtration occurs when pores are barely large enough to admit the contaminant molecule. As contaminants come in different sizes, they are attracted differently depending on pore size of the filter.

- **Chemical Properties**

The filter surface may actually interact chemically with organic molecules. Also electrical forces between the activated carbon surface and some contaminants may result in adsorption or ion exchange. Adsorption is also affected by the chemical nature of the adsorbing surface. The chemical properties of the adsorbing surface are determined to a large extent by the activation process. Activated carbon materials formed from different activation processes will have chemical properties that make them more or less attractive to various contaminants. For example, chloroform is adsorbed best by activated carbon that has the least amount of oxygen associated with the pore surfaces.

- **Contaminant Properties**

A general rule of thumb is that similar materials tend to associate. Organic molecules and activated carbon are similar materials; therefore there is a stronger tendency for most organic chemicals to associate with the activated carbon rather than staying dissolved in a dissimilar material like water. Generally, the least soluble organic molecules are most strongly adsorbed. Often the smaller organic molecules are held the tightest, because they fit into the smaller pores.

Water Temperature and pH

Adsorption usually increases as pH and temperature decrease. Chemical reactions and forms of chemicals are closely related to pH and temperature. When pH and temperature are lowered, many organic chemicals assume more adsorbable form.

Exposure Time

The process of adsorption is also influenced by the length of time that the activated carbon is in contact with the contaminant in the water. Increasing contact time allows greater amounts of contaminant to be removed from the water. Contact is improved by increasing the amount of activated carbon in the filter and reducing the flow rate of water through the filter.

Adsorption is caused by a type of van der waals force which exists between molecules. The force acts in a similar way to gravitational forces between planets. These Sources are extremely short ranged and therefore sensitive to the distance between the carbon surface and the adsorbate molecule. They are also be additive, meaning the adsorption force is the sum of all interactions between all the atoms. The short range and additive nature of these forces results in activated carbon having the strongest physical adsorption forces of any known material.

All compounds are adsorbable to some extent. In practice, AC is used for the adsorption of mainly organic compounds along with some larger molecular weight inorganic compounds such as iodine and mercury.

The adsorbability of a compound increases with:

- Increasing molecular weight

- A higher number of functional groups such as double bonds or halogen compounds.

- Increasing polarisability of the molecule.

This is related to electron clouds of the molecule (Ecologix Environmental System, 2006).

van der Waals force

Term **van der Waals force** refers to a particular class of intermolecular forces. The term originally referred to all such forces, and this usage is still sometimes observed, but it is now more commonly used to refer to those forces which arise from the polarization of molecules into dipoles.

Van der Waals bonding, also known as **London force, instantaneous dipole effect**, and **induced dipole interaction**, is an intermolecular force or interatomic force that causes an attraction between temporarily induced dipoles in nonpolar molecules and atoms because of assymetrical distribution of electrons due to their movement. Van der Waals bonding is much weaker than both ionic and covalent bonding, and usually weaker than hydrogen bonds. Van der Waals bonding is the sole process by which noble gases are attracted to each other, and the dominant form of interaction between electrically neutral species with all of their bonds saturated. Bonding by van der Waals forces occurs through *induced dipole* interactions. By contrast to dipolar molecules, which possess a small static dipole due to electronegativity differences between covalently bonded atoms, dipole oscillations are observed in all atoms and molecules (Wikipedia, 2006)

Applications in the water industry

The water industry uses activated carbon in several forms, typically powdered and granular, to deal with a variety of undesirable aspects in raw water. To the right is an image of pilot scale carbon columns at a water treatment plant.

Seasonal application of powdered activated carbon (PAC) at the raw water intake or rapid mix unit is used by some plants to correct short term raw water quality problems such as algal blooms. PAC is basically used to correct taste and odor problems which are primarily an aesthetic quality of the water. Other uses such as residual ozone destruction and chemical contamination prevention exist, but are not as well documented. Contact time is needed to allow adsorption to occur. The PAC is removed from the water by the processes of coagulation, flocculation, and sedimentation. Once the PAC has been separated from the water it is disposed of along with sedimentation sludge. Some non-traditional systems such as sludge-blanket clarifiers also use PAC.

Granular activated carbon is typically found in beds or filter columns as a Granular Activated Carbon (GAC) Cap and will treat water continuously when raw water quality problems exist year round. The GAC Cap is typically found above the filter media as a distinct layer. In some applications the sand layer can be replaced by GAC. When GAC is used for long term applications it can be more economical since

the carbon can be reactivated following decreased adsorption efficiency. If a GAC cap follows ozonation in the treatment process, a biological layer can be cultivated in the granular activated carbon cap. Since ozone disinfection leaves no residual disinfectant this biological layer is able to grow freely and metabolize some of the organics in the water, enhancing the overall removal by the GAC column
(Safety Emporium Laboraory and Safety Supplies, 2006).

2.3 Adsorption process

In this work, two models were used to fit the experimental data: Langmuir model and the Freundlich model.

2.3.1) The Langmuir equation

The Langmuir equation was chosen for the estimation of maximum adsorption capacity corresponding to biomass surface saturation. The linearised form of the above equation after rearrangement is given below:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{C_e}{q_{max}}$$

(Eq. 2.1)

where; K_L = a constant related to the adsorption/desorption energy $(dm^3\,g^{-1})$

q_{max} = the maximum sorption upon complete saturation of the adsorbent surface.

The experimental data were fitted into equation (Eq. 2.1) for linearisation by plotting C_e/q_e against C_e.

2.3.2) The Freundlich equation

The Freundlich model was chosen to estimate the adsorption intensity of the sorbent towards the adsorbent and the linear form is represented by equation (Eq. 2.2):

$$\ln q_e = \ln K_f + \frac{1}{n}\ln C_e$$

(Eq. 2.2)

where; q_e = the adsorbate uptake per unit weight of adsorbent (mg of adsorbate adsorbed/g adsorbent);

C_e = Concentration of adsorbate in solution at equilibrium (mg dm^{-3});

K_f and n = Freundlich constants.

The value of n indicates the affinity of the sorbent towards the adsorbent. A plot of ln C_e against ln q_e in equation (Eq. 2.2) yielding a straight line indicates the confirmation of the Freundlich adsorption isotherm. The constant $\frac{1}{n}$ and ln K_f can be determined from the slope and intercept respectively (Michael Horsfall et al., 2005).

2.6 Principle of photocatalysis process

A semiconductor, or TiO$_2$, combines two forms of broad band energy that are the occupied valence band (*vb*) and unoccupied conduction band (*cb*). These two bands are separated by the energy gap called the band-gap (E$_{bg}$). When TiO$_2$ is illuminated with near UV irradiation ($\lambda < 400$ nm) whose energy is equal to or higher than the band-gap energy, electrons from the valence band (*vb*) are promoted to the conduction band (*cb*) with the simultaneous generation of a hole (h^+).

$$TiO_2 + h\nu \rightarrow e^-_{cb} + h^+_{vb}$$ (Eq. 2.3)
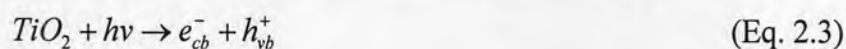
These photogenerated electron and hole pairs can react with the electron donors (D) or electron acceptors (A) that are adsorbed or close to the surface of TiO$_2$ as described in Figure 2.2
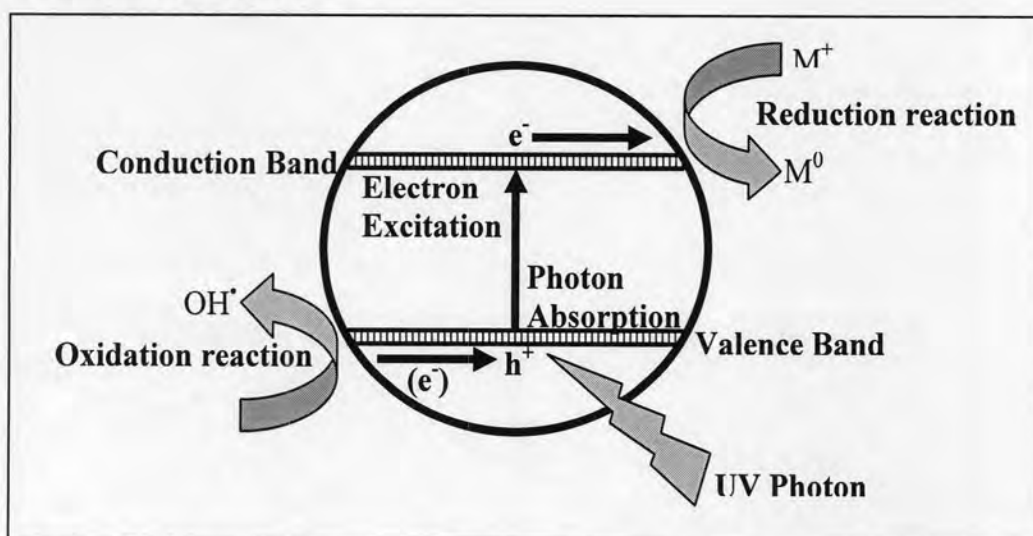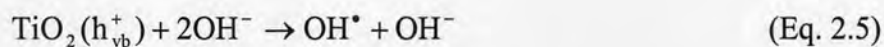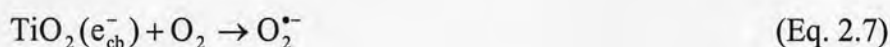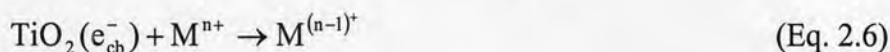

Figure 2.2 Schematic of the photocatalysis process (Linsebigler et al., 1995)

At the valence band (*vb*), the photogenerated holes can oxidize either the organic molecule directly or hydroxyl groups (•OH). These highly reactive radicals

are far stronger oxidizing agents than ozone and chlorine, both known as dioxide (CO_2) and water (H_2O) by these oxidation reactions.

$$TiO_2(h_{vb}^+) + H_2O \rightarrow OH^\bullet + H^+ \qquad \text{(Eq. 2.4)}$$

$$TiO_2(h_{vb}^+) + 2OH^- \rightarrow OH^\bullet + OH^- \qquad \text{(Eq. 2.5)}$$

On the other hand, the photogenerated electrons at the conduction band (*cb*) tend to combine with electron acceptors (A) such as metal ions already presented in the water. Thus the metal ions can be reduced to their harmless species. In addition, as the photogenerated electron capture by oxygen (O_2), super oxide anions radical ($O_2^{\bullet-}$) are also formed. The overall reduction reactions can be expressed by the following equations (Butler et al., 1993; Chan et al., 2001; Litter, 1999).

$$TiO_2(e_{cb}^-) + M^{n+} \rightarrow M^{(n-1)+} \qquad \text{(Eq. 2.6)}$$

$$TiO_2(e_{cb}^-) + O_2 \rightarrow O_2^{\bullet-} \qquad \text{(Eq. 2.7)}$$

2.4.1 Kinetic considerations in heterogeneous photocatalysis

The Langmuir-Hinshelwood model is widely used to analyze the disappearance rate of contaminants in water, especially in the presence of preadsorption or dark adsorption prior to illumination. The Langmuir adsorption model assumes that:

At equilibrium, the number of surface adsorption sites is fixed, then the only one substrate may bind at each surface site and the heat of adsorption for the substrate is identical for each site and is independent of surface coverage. After that, there is no interaction between adjacent adsorbed molecules then the rate of surface adsorption of the substrate is greater than the rate of any subsequent chemical reactions. Moreover, there is no irreversible blocking of active sites by binding to product. With these assumptions, the surface coverage, θ, is related to the initial concentration of the substrate, C, and to the apparent adsorption equilibrium constant, K, via the following equation:

$$\theta = \frac{KC}{(1+KC)} \qquad \text{(Eq. 2.8)}$$

The rate of product formation can then be written as a single-component Langmuir-Hinshelwood expression:

$$r = -\frac{dC}{dt} = \frac{kKC}{(1+KC)} \qquad \text{(Eq. 2.9)}$$

Where r represents the initial rate of disappearance of the contaminant, k is an apparent reaction rate constant which is related to the adsorption/desorption affinity, and K is the Langmuir constant reflecting the adsorption/desorption equilibrium between the reagent and the surface of the photocatalyst.

A convenient means of using this equation is to demonstrate linearity of the data when plotted as the inverse initial rate $(1/r)$ versus inverse initial concentration $(1/C)$:

$$\frac{1}{r} = \frac{1}{k} + \frac{1}{kKC} \qquad \text{(Eq. 2.10)}$$

with both slope $(1/kK)$ and intersept $(1/k)$ positive.

For low concentration of contaminants, the reaction rate is essentially of the first order:

$$r = kKC \qquad \text{(Eq. 2.11)}$$

In this performance, the apparent reactivity of a molecule is promote of two characteristics; the rate constant, k, and the Langmuir constant, K.

Normally, the highest efficiency of the photocatalytic degradation will be observed at a relatively high concentrations of substrate to satisfy the condition $KC >>> 1$ in Eq. 2.9 (Emeline et al., 2000). Turchi and Ollis (1990) reported that the apparent constant K represents different combinations of the Langmuir constant, carrier trapping constants, and surface reaction constants, all of which are important to achieve a higher efficiency for the photocatalyst. Cunningham and Al Sayyed (1990) have measured dark Langmuir adsorption isotherms for TiO_2 for a variety of different organic pollutants, and the values of K are significantly smaller than the values of K obtained from plots of $1/r$ versus $1/C$.

The rate constant, k, depends on the light intensity. At low intensity of photon, k scales linearly with light intensity, whereas at higher light intensity, it scales with the square root of the light intersity. From Eq. 2.11, as $KC >>> 1$, the reaction rate, r, is

dependent on k and, consequently, the light intensity. The dependence of reaction rate on light intensity can be illustrated as the following equations:

Low light intensity, $r \alpha\ I$ (Eq. 2.12)

High light intensity, $r \alpha\ I^{1/2}$ (Eq. 2.13)

Very high light intensity, $r \alpha\ I^0$ (independent) (Eq. 2.14)

Where I represents the incident light intensity.

Both explanations have been put forward for the square-root dependence. First, the carrier recombination is thought to dominate at the higher light intensities (Okamoto et al., 1985), and secondly, the occurrence of bimolecular recombination of •OH can also account for this dependence (Kormann et al., 1991). The independence of the reaction rate on a very high light intensity can be explained in terms of a diffusion limitation on the transport of the reagent molecules to the photocatalyst surface (Emeline et al., 2000)

2.6 Sol-gel technique used for TiO$_2$/AC preparation.

The sol-gel technique is a method used to synthesize oxide materials such as ceramic and glass. This preparation associates the transition of a system from sol, which is a stable suspension of colloidal solid particles within a liquid phase into gel, a porous 3-dimensionally interconnected solid network throughout a liquid phase (Pierre, 1998; Brinker, et al., 1990). Colloids are solid particles with diameters of 1-100 nm (Davis and Redeal, 1963). The sol-gel process consists basically a homogeneous solution of alkoxides, which are used as precursors under the hydrolysis and subsequently polymerization. When the extent of polycondensation and cross linking of polymeric molecules become extensive, the solution becomes rigid and a wet gel will form. The gel is converted into dense ceramic or glass materials with further drying and heat-treatment. In drying treatments, the wet gel converts to a xerogel through natural evaporation or an aerogel through supercritical drying (Brinker, C.J. et al., 1990).

In summary, the sol-gel process includes four steps: hydrolysis, polycondensation, drying, and thermal decomposition.
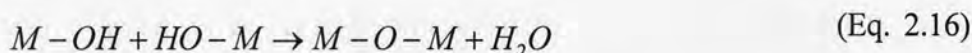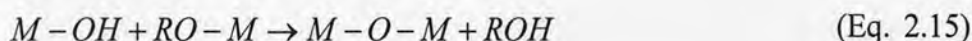
The general process for transformation of sol to gel can be described as following:

1. Hydrolysis of metal alkoxide

$$M - OR + H_2O \rightarrow M - OH + ROH \qquad \text{(Eq. 2.14)}$$

The M represents a metal, such as Si, Ti and Al, and R is an alkyl group then OR is an alkoxy group and ROH is an alcohol. The hydrolysis occurs when water is added to the alkoxide, which is usually dissolved in alcohol. During the initial reaction, usually referred to as pregelation, the reactants hydrolyze and condense to form gel.

2. Condensation of two partially hydrolyzed molecules to give a bridging oxygen or metaloxane group, M-O-M:

$$M - OH + RO - M \rightarrow M - O - M + ROH \qquad \text{(Eq. 2.15)}$$

$$M - OH + HO - M \rightarrow M - O - M + H_2O \qquad \text{(Eq. 2.16)}$$

In the condensation or polymerization reactions, alkoxy groups (-MOR) react with hydroxyl groups (-MOH), which was formed during the hydrolysis step, to form metaloxanes (-MOM-). It is important to note that during this step the primary structure and the properties of the gel are determined because these reactions increase the molecular weight of the oxide polymer.

2.6 2- Chlorophenol (2-CP)

2-CP represents important water pollutants and has been named as priority pollutant and has the effluent's standard less than 24.05 mg/L and the drinking water's standard less than 1 µg/L reported by the US EPA (M.A. Callahan, 1979). 2-CP has many synonyms that are o-chlorophenol, 2-hydroxychlorobenzene, 1-chloro-2-hydroxybenzene, o-chlorophenic acid, andchlorophenolate.

2-CP is present in drinking-water as a result of the chlorination of phenols, as by-products of phenoxy herbicides. 2-CP is normally found in wastewater from industry such as chemical, pulp and paper, petrochemical industry. The stability of the C-Cl bond in halohydrocarbons is responsible for their toxicity and persistence in the biological environment (Greenpeace Report, 1992; H. Roques et al., 1996).
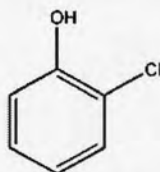
Figure 2.3 2-Chlorophenol

The main routes of entry of 2-CP to the aquatic environment are discharges from plants manufacturing it, or from plants, those employ it as intermediate in the production of higher chlorinated phenoxy herbicide. Indirect sources include discharges from paper mills as by-products of chlorine-based bleaching, as a result of disinfection of sewage and industrial wastewater with chlorine and from slow microbial breakdown of herbicides during post-application period. The compound is also used as a solvent for extracting sulfur and nitrogen compounds from coal (chemicalland21, 2006)

2-CP is very toxic and poorly biodegradable (N. N. Rao et al., 2003). A wastewater stream containing 2-CP over 200 mg/L may not be treated effectively by direct biological method (M.A. Callahan, 1979).

Oxidation of 2-CP under photocatalytic, electrocatalytic, Fenton's oxidation, and supercritical water oxidation (N. N. Rao et al., 2003) conditions has been reported.

- Physical data

The physical data of 2-CP as shown in Table 2.2

Table 2.2 Physical data of 2-CP

Physical data	
Molecular weight	128.56
Appearance	colourless to light brown
Melting point	7°C
Boiling point	176°C
Vapour pressure	2.2 mmHg at 20°C
Density (g cm^{-3})	63°C (closed cup)
Water solubility	2.85 g 100ml^{-1}

- Stability

Stable. Hygroscopic. Combustible. Incompatible with oxidizing agents, acid anhydrides, acid chlorides.

- Toxicology

Corrosive – causes burns. Very destructive of mucous membranes. Harmful of swallowed, inhaled or absorbed through the skin. Chronic exposure may cause liver, kidney or reproductive damage. Severe eye irritant.

Table 2.3 Toxicity data of 2-CP

Toxicity data	
ORL-RAT LD50	670 mg kg-1
ORL-MUS LD50	345 mg kg-1
IPR-RAT LD50	230 mg kg-1
SCU-RAT LD50	950 mg kg-1
SCU-RBT LDlo	950 mg kg-1

ORL = oral

IPR = intraperitoneal

SCU = subcutaneous

RAT = rat

MUS = mouse

RBT = rabbit

LD50 = lethal dose 50 percent kill

LDlo = lowest published lethal dose

- Environmental information

  Toxic to aquatic organisms – may cause long term damage in the environment.

- Personal protection

  Safety glasses, gloves, adequate ventilation

2.7 Degradation of 2-chlorophenol

It is generally accepted that, after band-gapirradiation in heterogeneous photocatalytic systems •OH is produced by direct hole oxidation of eithersurface-adsorbed water molecules or hydroxide ions. For aromatic substrates, it is well documented that •OH attack occurs mainly via addition to the aromaticring to yield a substituted hydroxycyclohexadienyl (HCHD) radical. Some authors consider that H-abstraction may also play an important role, and direct electron abstraction from the aromatic compoundby •OH to give a resonance-stabilized cationradical is also presumed to be of importance. On the basis of our results and the cited literature, the fol-lowing (simplified) mechanism can be proposed for the heterogeneous photocatalytic degradation of 2-CP (Fig. 2.4).
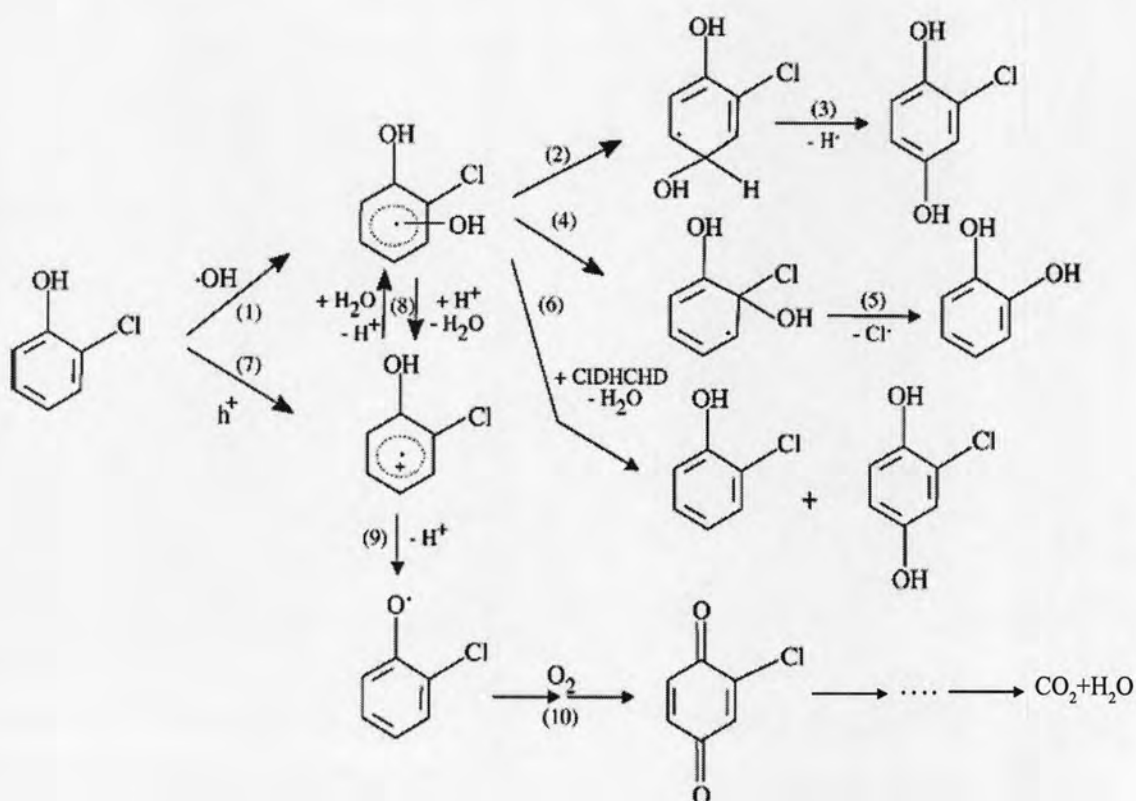

Figure 2.4 Simplified mechanism for the photocatalytic degradation of 2-CP (István Ilisz, 2002)

The addition of •OH to the aromatic moiety (1) leads to the formation of chlorodihydroxycyclohexadienyl radical (ClDHCHD). •OH addition in the *para* position to 2-CP (2), followed by H-abstraction (3), leads to ClHQ, while addition in *ortho* position (4), followed by Cl-abstraction (5), gives PC. Based on the experimental results that ClHQ and PC have similar degradation rates, the measured concentration ratio of ca. 5:1 suggests a highly favored addition of •OH in the *para* position, followed by H-abstraction. The ClDHCHD radical formed in the first step may disproportionate into 2-CP and ClHQ, accompanied by water elimination (6). Although •OH often seems to be a plausible explanation for heterogeneous photocatalytic transformations observed in the aqueous phase, the possibility of direct hole oxidation can not be excluded. Since direct electron transfer from 2-CP to a semiconductor (7) can also give a positive radical, which can be converted into an ClDHCHD radical after nucleophilic water addition (8), or into chlorophenoxyl radical after deprotonation (9). (In the presence of dissolved O_2 the chloro phenoxyl radical may lead to the formation of quinonic derivatives (10).

Since the hydroxylation initiated by either •OH or a surface trapped hole can lead to ClDHCHD, a distinction between direct hole and •OH oxidation can hardly be accomplished by using only the product distribution.

Further oxidation of the aromatic intermediates leads to ring opening and aliphatic products may occur (e.g. carboxylic acids and hydroxylated carboxylic acids). Prolonged irradiation will lead to the total mineralization, producing water, carbon dioxide and hydrochloric acid as final products (István Ilisz, 2002).

2.8 Synthesis and application of TiO_2/AC

Titanium dioxide (TiO_2) is widely use in photocatalytic degradation that is TiO_2/UV technique can lead to effective removal of soluble organic matter. But, TiO_2 has low adsorption activity that lead to low photocatalytic degradation efficiency. In 2003, the photocatalytic degradation was carried on using commercial TiO_2, and mixtures of this semiconductor with different AC suspended solution by Silva et al. (Silva et al., 2003). In the same year, TiO_2 was enhanced by immobilized on AC filter and Ao and Lee discovered that TiO_2 immobilized on AC filter was less affected by the increasing humidity levels and have knowledge that the use of AC acted as a local

pollutant concentrator by adsorbing pollutants from the air stream and thereby diffused to the TiO_2 for photodegradation (Ao and Lee, 2003). In 2004, Amjad H. Sheikh et al., was studied three different techniques for synthesize TiO_2/AC that are chemical vapour deposition (CVD), direct air-hydrolysis (DAH), high temperature impregnation (HTI) (Amjad et al., 2004), and in the same year, Dong-Keun Lee was studied the sol-gel technique for synthesized TiO_2/AC and he concluded that among 4 techniques, the sol-gel technique is the most common method of producing TiO_2/AC composite (Dong-Keun Lee et al., 2004).

In the next time, there are many application of TiO_2/AC composite such as C.H. Ao and S.C. Lee was studied to examine the effect of TiO_2 immobilized on AC by co-injecting binary pollutants (Ao and Lee, 2004). And in 2005, they were studied to enhance effect of using TiO_2 immobilized on AC (TiO_2/AC) filter for removal indoor air pollutant to further evaluate the TiO_2/AC filter for practical application (Ao and Lee, 2005).

TiO_2-coated granular activated carbon was employed for the removal of toxic microcystin-LR from water. Surface areas of the activated carbon in the vicinity of TiO_2 particles provided sites for the adsorption of microcystin-LR, and the adsorbed microcystin-LR migrated continuously onto the surface of TiO_2 particles which were coated mainly at the exterior surface in the vicinity of the entrances of the macropores of the activated carbon. The migrated microcystin-LR was finally degraded into nontoxic products and CO_2 very quickly. These combined roles of the activated carbon and TiO_2 showed a synergistic effect on the efficient degradation of toxic microcystin-LR (Dong-keun Lee et al., 2004), From this information, it was show the benefit of the combined of the activated carbon and TiO_2 and this technique was chosen to use in this work.

The synthesized technique of this work was adapted from the sol-gel technique of Dong-keun Lee, 2004. TiO_2 were mixed with AC, then the hydrolysis and polymerization were form as sol. After that the polymeric was very tight and occurred in the wet gel form. Drying at room temperature, the xerogels were formed and the structure of TiO_2 was formed when calcined at 500°C. In the research of Dong-keun Lee the molar ratio of TiO_2/AC was 1:33. Therefore, in this work

TiO$_2$/AC was prepared with the ratio of TiO$_2$ to AC as 0:1, 1:10, 1:33, 1:50, 1:70, 1:100, and 0:1 in the molar ratios of TiO$_2$/AC composite.