CHAPTER II

BACKGROUNDS AND LITERATURE REVIEW

2.1 Photocatalysis process

2.1.1 General information

Photocatalysis process is one of the new "Advanced Oxidation Processes" (AOPs) (Andreozzi et al., 1999), which has been applied successfully to purify water streams containing organic, biological and inorganic pollutants. This process offers a number of advantages over conventional techniques such as activated carbon or chemical precipitation that only transfer the pollutants from one phase to another. By this way, the pollutants are degraded or transformed into less harmful substances (Huang et al., 1993; Litter, 1999).

The photocatalysis process is dependent on the double ability of the catalyst to adsorb both pollutants on it surfaces and absorb light with an appropriate wavelength (Herrmann, 1999). Various types of semiconductor, such as TiO_2, ZnO, CdS, WO_3, ZnO_2 and Fe_2O_3, have been used as the catalysts in photocatalysis process. From the available semiconductors, ZnO is generally unstable with respect to incongruous dissolution yielding $Zn(OH)_2$ on the ZnO particle surfaces, and WO_3, although useful in the visible range, is less photocatalytically active than TiO_2 (Litter, 1999). It has been indicated that TiO_2 is the most useful material due to its interesting qualities of high stability, high photocatalytic activity, non-toxicity and inexpensive (Barbeni et al., 1985; Yu et al., 1998).

According to the interesting characteristic of TiO_2, the photocatalysis with TiO_2 for the degradation of organic and inorganic air and water pollutants has been received considerable attention (Rajeshwar et al,. 1995). On the basis of the generation of highly oxidative holes, a variety of aliphatic and aromatic compounds such as carbofuran are completely mineralized (Tennakone et al., 1997).

Besides, bacterial pollutants can be removed and detoxified via this process (Dunlop *et al.*, 2002; Herrera Melián *et al.*, 2000).

2.1.2 Principle of photocatalysis process

A semiconductor, or TiO_2, combines two forms of broad band energy that are the occupied valance 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 ($\lambda < 400nm$) whose energy is equal to or higher than the band-gap energy, electrons from the valance band (*vb*) are promoted to the conduction band (*cb*) with the simultaneous generation of a hole (h^+).

$$TiO_2 + h\nu \longrightarrow e^-_{cb} + h^+_{vb} \qquad (2.1)$$
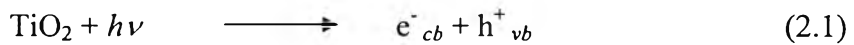
These photogenerated electron and hole pairs can react with the electron donors (D) or electron acceptors (A) that are adsorbed or close to the surface of TiO_2 as described in Figure 2.1.
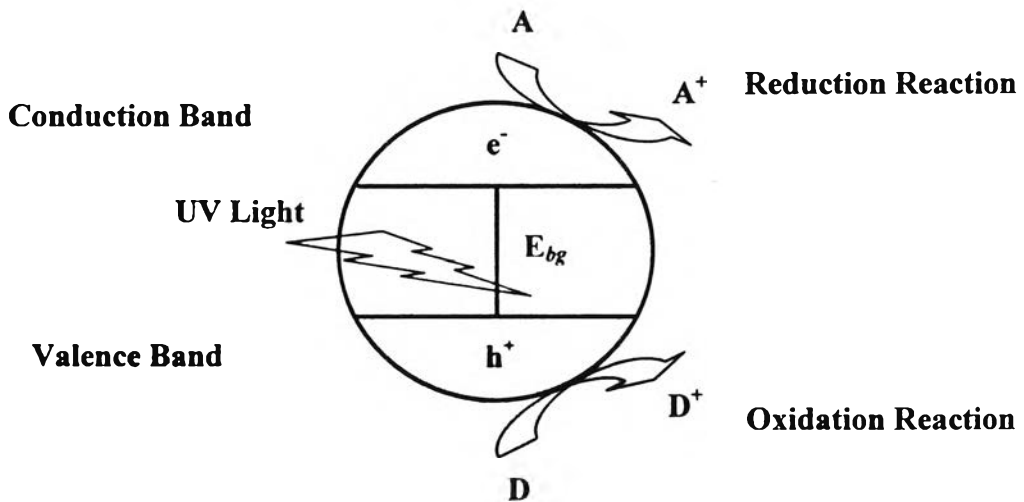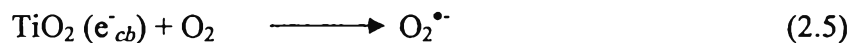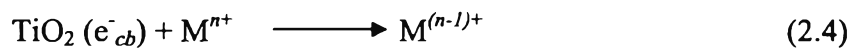

Figure 2.1 Schematic of the photocatalysis process (Cai *et al.*, 2003).

At the valance band (*vb*), the photogenerated holes can oxidize either the organic m olecule d irectly or h ydroxyl groups (OH^-) a nd t he w ater m olecule (H_2O) adsorbed onto the TiO_2 surface to hydroxyl radicals ($OH^\bullet$). These highly reactive radicals are far stronger oxidizing agents than ozone and chlorine, both known as strong oxidants. The organic pollutants are mineralized or degraded into carbon dioxide (CO_2) and water (H_2O) by these oxidation reactions.

$$TiO_2\ (h^+_{vb}) + H_2O \longrightarrow OH^\bullet + H^+ \qquad (2.2)$$

$$TiO_2\ (h^+_{vb}) + 2OH^- \longrightarrow OH^\bullet + OH^- \qquad (2.3)$$

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; Litter, 1999; Chan *et al.*, 2001).

$$TiO_2\ (e^-_{cb}) + M^{n+} \longrightarrow M^{(n-1)+} \qquad (2.4)$$

$$TiO_2\ (e^-_{cb}) + O_2 \longrightarrow O_2^{\bullet-} \qquad (2.5)$$

2.2 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 f orm h as widely a pplication t han t he r utile f orm (Augustynski, 1993). T he structure o f rutile a nd a natase c an b e d escribed i n t erms o f t etragonal s tructure, a s indicated in Figure 2.2 and their properties are shown in Table 2.1.

Rutile $d_{Ti-O}^{eq} = 1.949\,\text{Å}$ Anatase $d_{Ti-O}^{eq} = 1.934\,\text{Å}$

$d_{Ti-O}^{AP} = 1.980\,\text{Å}$ $d_{Ti-O}^{AP} = 1.980\,\text{Å}$

$a = 4.593\,\text{Å}$ $a = 3.784\,\text{Å}$

$c = 2.959\,\text{Å}$ $c = 9.515\,\text{Å}$

$Eg = 3.1\,eV$ $Eg = 3.3\,eV$

$\rho = 4.250\,g/cm^3$ $\rho = 3.894\,g/cm^3$

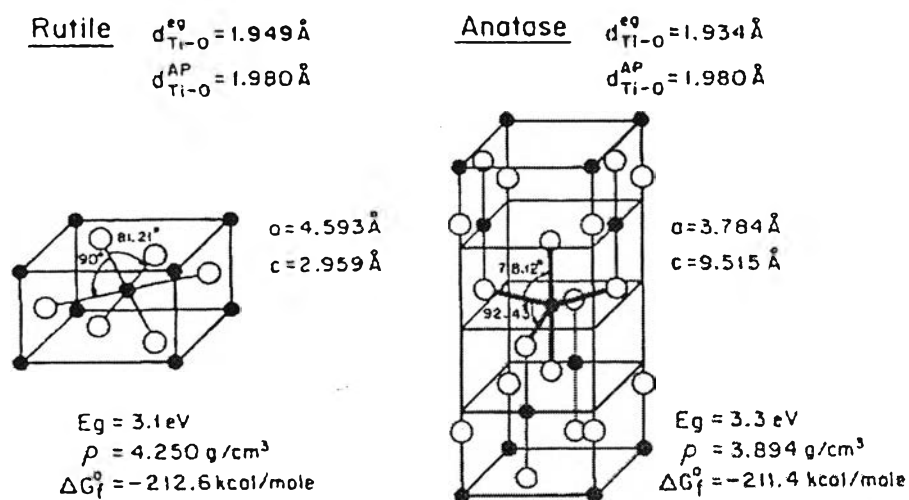$\Delta G_f^0 = -212.6\,kcal/mole$ $\Delta G_f^0 = -211.4\,kcal/mole$

Figure 2.2 Structure of rutile and anatase TiO_2 (Linsebigler *et al.*, 1995).

Table 2.1 Properties of rutile and anatase (Fujishima *et al.*, 1999; Litter, 1999).

Property	Rutile	Anatase
Crystalline form	Tetragonal	Tetragonal
Band gab energy (eV)	3.030	3.200
Hardness (Mohs)	6.0-7.0	5.5-6.0
Density (g/cm³)	4.250	3.894
Gibbs free energy, ΔG_f°	-212.6	-211.4
(kcal/mole)	4.593	3.784
Littice constant, a (A°)	2.959	9.515
Littice constant, c (A°)	1858°C	Changes to rutile at
Melting point		high temperature
		~800°C

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 *et al.*, 2002).

In conventional photocatalysis process, TiO_2 is widely used as suspended form. Although it can be used to remove the pollutants efficiently, the post-treatment such as the separation is required. This limitation can be overcome by immobilizing TiO_2 particles as thin films on a solid substrate. Many techniques such as chemical vapor deposition (CVD), spin-coating and sol-gel technique are proposed to immobilize TiO_2 (Ding et al., 2001; Srikanth et al., 2001). Among these techniques, the thin film TiO_2 is normally prepared using a sol-gel technique (Kim et al., 1994).

Fretwell et al. (2001) prepared a thin film of TiO_2 using the sol-gel method by dip coating and spin coating. The sol contained 5 g of TTiP, 40 ml of ethanol, 2.5 g of PEG600 and 2.5g of DEG. Films from dip-coated and spin-coated were calcined at 450°C for 30 min in furnace. Photocatalytic activities of both films were not different.

2.3 Sol-Gel Technique

2.3.1 General principles of sol-gel processing

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). 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 becomes 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 et al., 1990).

In the preparation of TiO_2 thin film, the sol solution is prepared via pathway A. After hydrolysis and polymerization, sol is deposited on a substrate by dip coating technique. Finally, the obtained film is dried and required further heat treatment for

crystallization as most gels are amorphous to get the thin film as illustrated in Figure 2.3.
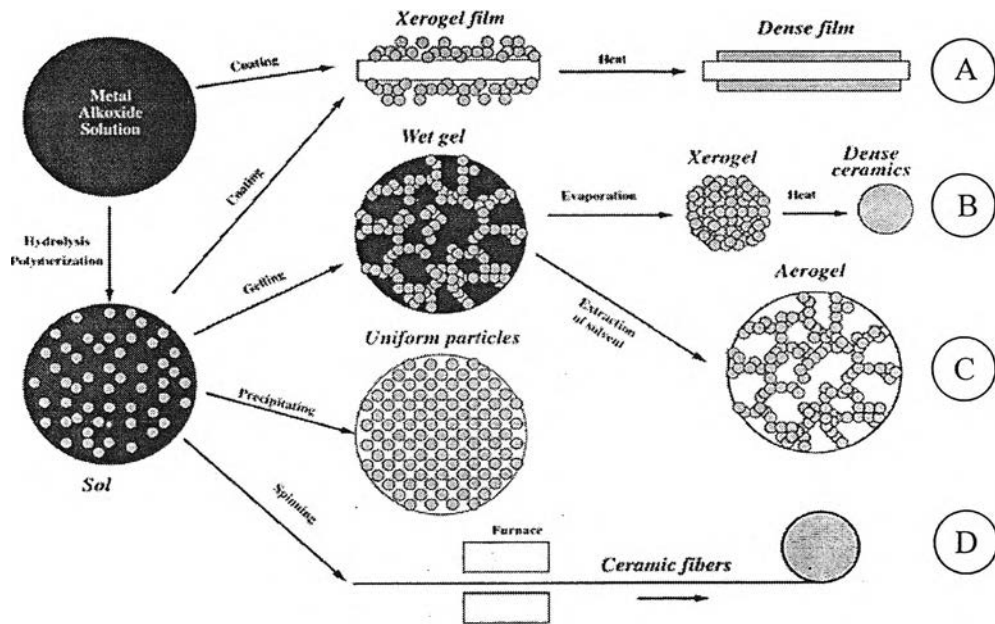

Figure 2.3 Diagram of sol-gel process.

The sol-gel technique is the most widely used to prepare various functional coating films because of its advantages over conventional film formation techniques: good homogeneity, large area coating and good photocatalytic properties (Brinker *et al.*, 1990; Klein, 1991; Yu *et al.*, 2001).

2.3.2 Parameters influencing thin film property

The quality of TiO_2 thin films obtained from this technique is controlled by the type of metal alkoxide, solvent to alkoxide ratio, type of catalyst, additive substrate and calcination temperature (Arabatzia *et al.*, 2002; Vicente *et al.*, 2001; Yu *et al.*, 2001). The effects of these parameters are reported as follows:

2.3.2.1 Type of precursor

The precursor used in sol-gel is the metal alkoxide, which is an organic compound (alkoxy group) mostly having bond with metallic atom (M). The examples

of alkoxides commonly used in sol-gel processing are listed in Table 2.2. These alkoxides react at different rates according to the electronegativity of the cation (Bradley *et al.*, 1978). For example, monomeric alkoxides promote higher rates of hydrolysis and condensation reactions than oligomeric alkoxides because it is less static hindrance (Ulrich, 1988).

The $Ti(OC_3H_7^i)_4$ dissolved in isopropyl alcohol provides the formation of larger particles in the sol and a rough surface of the coating films because it has higher reaction rates of hydrolysis and condensation than $Ti(OC_2H_5)_4$ dissolved in ethanol (Hu *et al*,. 1992).

Table 2.2 Common alkoxides for sol-gel processing (Bradley *et al.*, 1978).

Name	Formula	Formula weight (g)	Density at 20°C (g/cm³)
Tetraethyl orthosilicate	$Si(OC_2H_5)_4$	208	0.936
Trimethyl borate	$B(OCH_3)_3$	104	0.915
Aluminum *sec*-butoxide	$Al(OC_4H_9)_3$	246	0.967
Titanium isopropoxide	$Ti(OC_3H_7)_4$	284	0.955
Zirconium isopropoxide	$Zr(OC_3H_7)_4$	327	1.05

The metal alkoxides are widely used as precursors as it has the reaction with water rapidly as described in terms of two separated reactions as follows (Klein, 1997):

$$\text{Hydrolysis:} \quad -MOR + H_2O \longrightarrow -MOH + ROH \qquad (2.6)$$
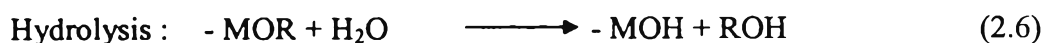
The M represents a metal, such as Si, Ti and Al, and R is an alkyl group then OR is an alkoxy group and ROH is an alcohol. The hydrolysis occurs when water is added to the alkoxide, which is usually dissolved in alcohol. During the initial reaction, usually referred to as pregelation, the reactants hydrolyze and condense to form gel.

Condensation : - MOH + ROM - ⟶ - MOM - + ROH   (2.7)

or - MOH + HOM - ⟶ - MOM - + H_2O (2.8)
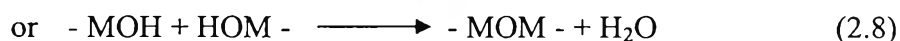
In the condensation or polymerization reactions, alkoxi groups (-MOR) react with hydroxyl groups (-MOH), which was formed during the hydrolysis step, to form metaloxanes (-MOM-). It is important to note that during this step the primary structure and the properties of the gel are determined because these reactions increase the molecular weight of the oxide polymer.

2.3.2.2 Type of solvent

Type of solvent affects on the morphology of the film surface. The solvent, which is highly volatile, enhances the smoothness of the film. As reported by the previous study, the film prepared from ethanol result in the more smooth film and fewer cracks than other solvents such as isopropanol. (Kajihara, *et al.*, 1999; Rookpun *et al.*, 2003). These events were also explained by Hu *et al* (1992). When adding ethanol to coating solution, the rate of hydrolysis and condensation of metal alkoxide were slower than adding isopropanol. The higher reaction rates result in the formation of larger particles in the sol and a rough surface of the film. On the other hand, the lower reaction rates gave rise to the formation of columnar particles in the sol and a smooth surface of the film.

The TiO_2 gel film prepared using isopropyl alcohol and 2-ethoxyethanol a s s olvent p recipitates t he a natase p hase a t l ow t emperature (350°C-400°C), while the film prepared from ethanol exhibited the higher crystallization temperature at 450°C (Hu *et al,.* 1992). Beside, the use of diethanolamine as solvent promotes the precipitation of both anatase (400°C) and rutile (650°C) phases out of TiO_2 coating films (Takahashi *et al.*, 1988).

2.3.2.3 Additive substance (acetylacetone)

Liu *et al.* reported preparation of TiO_2 thin films on NiTi surgical alloy using titanium(IV) butoxide : ethylene glycol monomethyl ether : ethyl acetoacetate : H_2O at a ratio of 1:20:1:4. In this preparation, a small amount of HNO_3 was added into the solution as a catalyst. The films were annealed in air at $500^{\circ}C$ for 1 h. The results showed that the solution at pH 1-2 in the presence of ethyl acetoacetate was stable and homogeneous. The resultant films were uniform, compact and smooth (Liu *et al.*, 2003).

The effects of complexing agents (CA), such as acetylacetone, diethanolamine and polyethylene glycol, on the anatase to rutile phase transition during the heat-treating of TiO_2 films were investigated (Djaoued *et al.*, 2002). TTIP : ethanol : H_2O : CA were employed in the preparation of coating solutions. The X-ray measurements indicated that the phase transition temperature strongly depends on the complexing agent present in the solution. Diethanolamine and polyethylene glycol promotes the anatase to rutile transition at $750^{\circ}C$ and $800^{\circ}C$ respectively, while acetylacetone seems to stabilize the anatase phase even at temperature as high as $900^{\circ}C$. Moreover, the size of the crytallites in TiO_2 films increases as the temperature increases.

A TiO_2 sol-gel synthesis using alkoxide Ti(O-Bu)$_4$, dissolved in n-butanol, in presence of acetylacetone as a chelating agent and acetic acid. The optimization of the mole ratio allowed a stability control up to two months. With this experimental method of coating, the good quality of the resulting thin films can be observed with no crack (Legrand-Buscema *et al.*, 2002).

Synthesis of sol-gel process derived nanophase TiO_2 films from titanium isopropoxide in ethanol, in the presence of stabilizing agents, diethanolamine, acetic acid and acetylacetone was performed. Crack free films with good adherence and quality were obtained from this route. The topographical information obtained from the AFM and SEM micrographs was correlated directly to the ion storage capacity (ISC). The larger gain size observed for the acetylacetone

derived film resulted in a lower ion storage capacity (ISC) and cathodic peak current for the film owing to the difficult diffusion in an relatively more ordered film (Verma *et al.*, in press).

2.3.2.4 Influence of calcination temperature

The calcination temperature strongly effect on the properties of TiO_2 such as relative portion of anatase and rutile in the film, surface area, porosity and crystal size. Moreover, different techniques to make TiO_2 such as chemical vapor deposition, thermal oxidation of Ti metal, and sol-gel method, yield different effects of calcination temperature. For example, for TiO_2 prepared by sol-gel methods, rutile begins to appear at a calcination temperature of 800°C in TiO_2 films on SnO_2-covered Vycor glass (Yoko *et al.*, 1991), while rutile appears at 720°C (Yoko *et al.*, 1987), 700°C (Kato, 1991), and 500°C (Tunsei *et al.*, 1991) in powder TiO_2. The Degussa P25 begins to transform to rutile at 600°C (Mills *et al.*, 1993).

In addition to surface area, porosity, crystal size and the ratio between anatase and rutile are also affected by changing in calcination conditions. As a result, calcination temperatures are an important parameter affecting the efficiency of photocatalytic reaction (Yoko *et al.*, 1991).

2.3.2.5 Influence of coating cycles

A novel strategy for the effective electron-hole separation in the thin film TiO_2 electrode prepared by sol-gel method has been presented. Films with thickness smaller than the space charge layer showed a larger photocurrent than films with thickness larger than the space charge layer. It is concluded that the increase in photocurrent is due to the effective electron-hole separation throughout the whole film thickness and the reduction of bulk recombination (Takahashi *et al.*, 2001).

The coloration phenomenon of the TiO_2 films strongly depends on the film thickness. As the thickness of TiO_2 films increases up to more than 1 µm, the

coloration becomes indistinct, while the films remain still transparent (Yu *et al.*, 2001).

The coating cycles effect on the thickness and uniformity of the TiO_2 film. According to the photodegradation of bisphenol-A (BPA), the concentration of BPA decreased as the coating cycles increased because of the increasing of the TiO_2 quantities (Lee *et al.*, 2004).

2.4 Application of photocatalysis on environmental abatement

The oxidation of *p*-hydroxybenzoic acid using UV radiation and TiO_2/UV radiation has been studied. The results indicated that the kinetics for both systems can be fitted by a pseudo-first-order kinetic model. The second oxidation process can be explained in terms of the Lanhmuir-Hinshelwood kinetic model. The kinetic rate constants for the TiO_2/UV system were greater (between 220-435%) than those obtained in direct UV photooxidation (De Heredia *et al.*, 2001).

Epling *et al.* (2002) investigated the retardation effects that result from the presence of ionic species, organic solvents and humic substances on the photo-bleaching of dyes. The results showed that HCl exhibited the strongest inhibition effect on both cationic and anionic dyes. HNO_3 and $NaHCO_3$ inhibited photo-bleaching of anionic dyes, but seemed to accelerate photo-bleaching of cationic dyes. In addition, natural humic substances, acetonitrile and alcohols were also found to have significant retardation effects on the photo-bleaching of dyes.

The photocatalytic degradation of pentachlorophenol using TiO_2 catalysts was investigated. The catalysts prepared by the sol-gel method used different gelation pH values and different calcination temperatures. The coating solutions consisted of titanium(IV) ethoxide, H_2O and different hydrolysis catalysts (3-HCl, 5-CH_3COOH, 9-NH_4OH) which were carried out at different pH values. It was found that the reaction followed a first-order reaction and the kinetic constant values changed slightly with the pH of gelation and more significantly with the calcination temperature (Pecchi *et al.*, 2001).

The mechanism of phenol photocatalytic decomposition and its intermediates in the presence of illuminated TiO_2 were also studied by Sobczyński et al., (2004). While illuminating TiO_2, they found that the major intermediates were hydroquinone, p-benzoquinone and catechol. After completion of the reaction, only four compounds; carbondioxide, water, formic acid and acetic acid, were identified. In addition, the reaction of phenol decomposition showed a first-order behavior.

2.5 Chromium

2.5.1 Properties of Chromium

Chromium is naturally occurring element found in rocks, animals, plants and soil. Chromium exists in two oxidation states, Cr(III) and Cr(VI). The Cr(III) state is considered one of the essential elements for living organisms, whereas Cr(VI) state is generally produced by industrial processes. Chromium is introduced into natural bodies of water from industries like electroplating, leather tanning, cement industries, steel industries and photography (Tel et al., 2004). Cr(VI) is thermodynamically stable as the anions chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$), which are soluble in aqueous solutions. Cr(III) is insoluble in water. Therefore, the separation and preconcentration of chromium species are required. In industry, chemical precipitation is an effective treatment technology which involves reduction of Cr(VI) to Cr(III) prior to precipitation and sedimentation (Ku et al., 2001). However, Cr(III) sludge is considered to be a hazardous waste that is difficult to dispose of.

2.5.2 Toxicology

The health effects associated with exposure to chromium are dependent on its oxidation state. The hexavalent form or Cr(VI) is considered a potential lung carcinogen. Cr(VI) can cause adverse effects on human health via many routes that can be described as follows (NSC, 1998; ATSDR, 2001):

Skin : Skin contact with certain Cr(VI) compounds can lead to skin ulcerations and dermatitis. It is also possible to develop an allergic reaction to the compound following exposure by any routine.

Eyes : Direct eye contact with chromic acid or chromate dusts can cause permanent eye damage.

Inhalation : Breathing high levels of Cr(VI) can result in irritation to the nose such as runny nose, nosebleeds, ulcers and holes in the nasal septum.

Ingestion : Ingesting large amounts of Cr(VI) can cause stomach upsets, ulcers, convulsions, kidney, liver damage and even death.

2.5.3 Chromium removed using photocatalysis process

The parameters effecting on the photocatalytic process are already investigated. For example, Weng *et al.* (1997) investigated the adsorption of Cr(VI) onto TiO_2. The results showed that the pH of solution was the key factor affecting the adsorption characteristics. The Cr(VI) adsorption was favorable under acidic conditions and the adsorbed quantity decreased with increasing pH and surface loading. Besides, decreasing temperature and ionic strength resulted in increasing adsorption capacity.

Chenthamarakshan *et al.* (2000) studied the effects of protons and ammonium ions on the photocatalytic reduction of Cr(VI). The results showed that both protons and ammonium ions enhanced the photoreduction of Cr(VI). The reduction kinetics switched from first order to zero order as the proton concentration was increased. Ammonium ions were also shown to exert a dramatic accelerating influence on Cr(VI) reduction, due to their behavior as the hole scavengers.

Schrank *et al.* (2002) studied photocatalytic reactions using Cr(VI) and dye in single and mixed systems. In the single system, both Cr(VI) and dye were degraded in acidic pH. In neutral pH, Cr(VI) was not reduced, while dye was almost completely

oxidized by both acidic and neutral conditions. In the mixed system, the reduction of Cr(VI) was faster than in the single system as dye was oxidized by photo-excited holes that prevented electron-hole recombination and promoted photoreduction of Cr(VI) on TiO_2. On the other hand, the oxidation of dye was also faster in the mixed system than in the single system as a result of the prevention of electron-hole recombination by Cr(VI).

Watcharenwong (2003) investigated the effects of pH, TiO_2 dosage, organic and inorganic additives on the photocatalysis of Cr(VI) from synthetic wastewater. The initial Cr(VI) concentration was 50 ppm and 3 g of TiO_2 powder was applied into the reactor. The results showed that the optimum pH for Cr(VI) removal under UV-irradiation was at pH 3 with 59.40% Cr(VI) removal efficiency. In the presence of formate ions, the efficiency was enhanced to 82.46%.