# CHAPTER II

BACKGROUNDS AND LITERATURE REVIEW

2.1 Chromium

Chromium is a naturally occurring element found in animals, rocks, plants, soil, and in volcanic dust and gases. Chromium is present in the environment in several different forms. The most common forms are chromium (0), chromium (III), and chromium (VI). All of chromium does not have taste or odor. Chromium (III) occurs naturally in the environment and is an essential nutrient. Chromium (VI) and chromium (0) are generally produced by industrial processes. The metal chromium, which is the chromium (0) form, is used for making steel. Chromium (VI) and chromium (III) are used for chrome plating, dyes and pigments, leather tanning, and wood preserving. The toxicity of chromium; breathing high levels of chromium (VI) can cause irritation to the nose, such as runny nose, nosebleeds, and ulcers and holes in the nasal septum. Ingesting large amounts of chromium (VI) can cause stomach upsets and ulcers, convulsions, kidney and liver damage, and even death. Skin contact with certain chromium (VI) compounds can cause skin ulcers. Allergic reactions consisting of severe redness and swelling of the skin have been noted. Then, many federals of many country realize to the hazardous of chromium for example EPA has set a limit of 100 µg chromium (III) and chromium (VI) per liter of drinking water (100 µg/L).The Occupational Safety and Health Administration (OSHA) has set limits of 500 µg water soluble chromium (III) compounds per cubic meter of workplace air (500 µg/m³), 1,000 µg/m³ for metallic chromium (0) and insoluble chromium compounds, and 52 µg/m³ for chromium (VI) compounds for 8-hours work shifts and 40-hours work weeks (Benoit, 1986).

Table 2.1 The property of chromium in the wastewater (Rai et al., 1987)

Oxidation State	Oxide	Cation	Anion	Characteristics
6	CrO_3	-	CrO_4^{2-} (chromate) $Cr_2O_7^{2-}$ (dichromate)	oxide acidic anions stable
3	Cr_2O_3	Cr^{3+} (hydrated)	$[Cr(OH)]^{3-}$ (chromate)	oxide amphoteric cation stable
2	(CrO)	Cr^{2+} (hydrated)	-	oxide basic, cation easily oxidized

Generally, the form of chromium (VI) in the solution is CrO_4^{2-} or $HCrO_4^-$. These forms depend on pH value and the concentration of chromium solution.
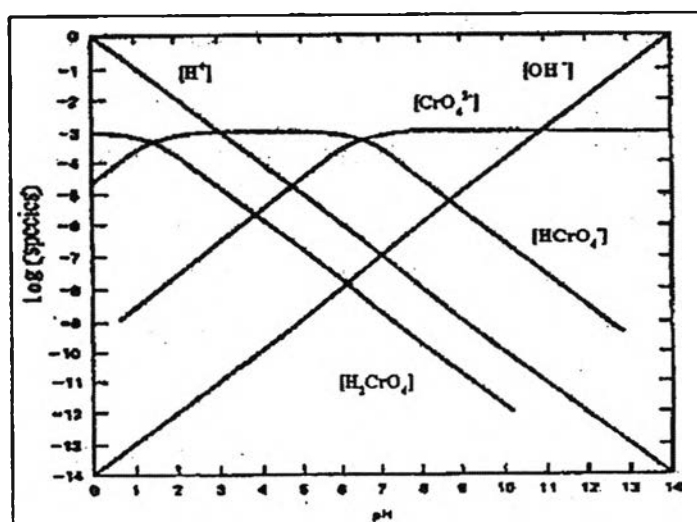
Figure 2.1 The scattered chromium in the varied pH solution (Ku and Jung, 2001)
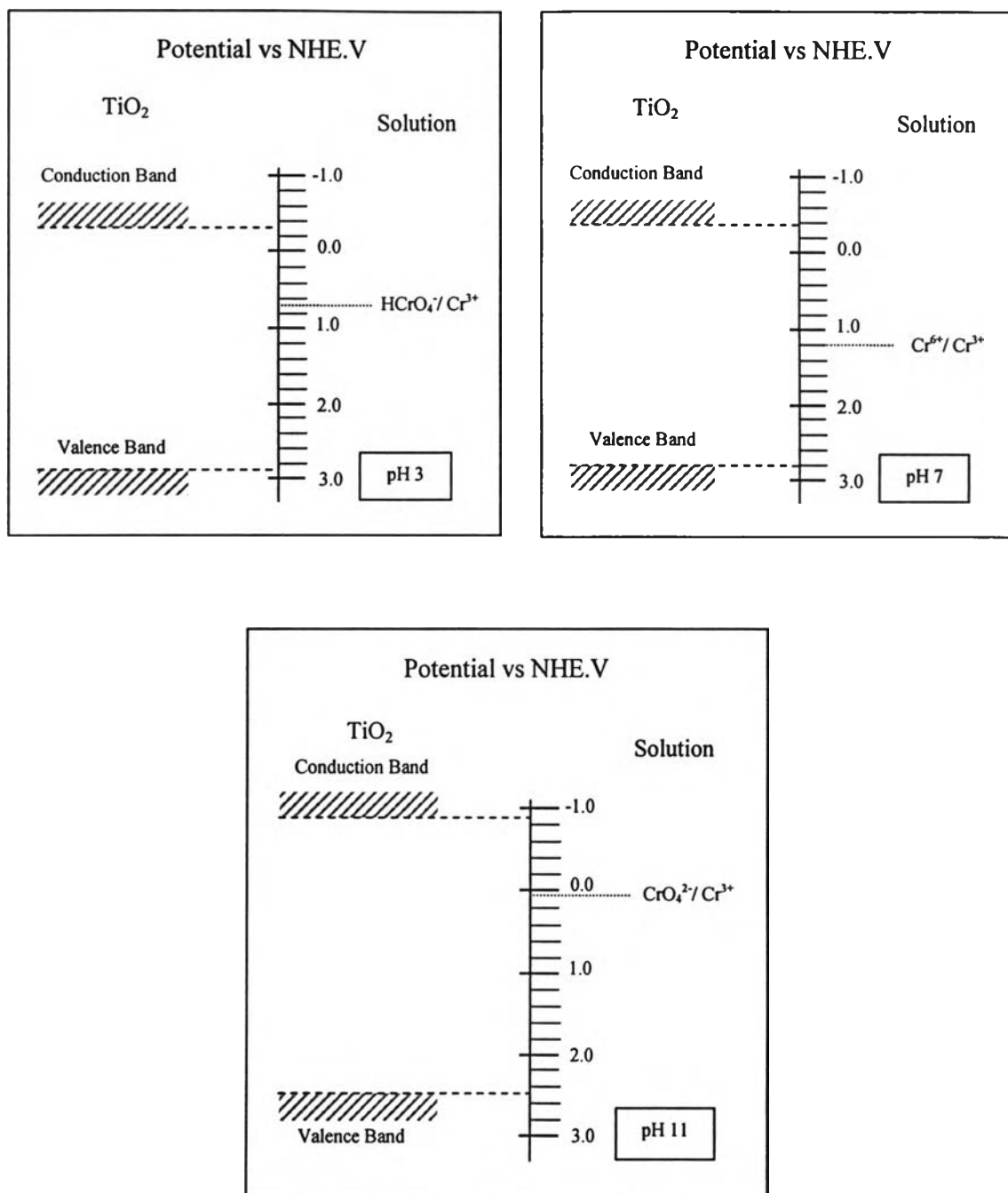
Figure 2.2 Diagram shows the potential of TiO_2 and chromium at pH 3, pH 7 and pH 11. (Adapted from Chenthamarakshan et. al., 2000)

2.2 Photocatalytic process

Photocatalytic process is applied in a large variety of reactions. For instance, total oxidations, dehydrogenation, hydrogen transfer, deuterium-alkane isotopic exchange, metal deposition, water detoxification, and gaseous pollutant removal (Herrmann et al., 1999). In the two latter points, it can be considered as one of the new 'advanced oxidation technologies' (AOT) for air and water purification treatment. Photocatalysis can be defined as "a catalytic reaction involving light absorption by a catalyst or a substrate" (Ding et al., 2001). Other definitions are as follow: "Catalysis is the action of a catalyst"; and a "Catalyst" (CdS, TiO_2, ZnO, WO_3 and ect.) is a substance that increases the rate of reaction without modifying the overall standard Gibbs energy change in the reaction" (Herrmann, 1999) The basic principles of photocatalytic process are the adsorption of substrates on catalytic surfaces and the irradiation process.

2.2.1 The adsorption

The adsorption process consists of physical force (Vander Waal's Force and Electrostatic Force) and chemical force.

The Vander Waal's Force is the attraction of free atoms or the neutral molecules. This phenomenon can appear cause of free driving of electron effect to the density of electrons in atoms or molecules are not stable and these promote the polar atom or molecule. Thus, adsorption is able to appear. Vander Waal's Force has low efficiency for attract another so the desorption is not difficult to occur and this point is the benefit for regeneration of the adsorbent. In addition, adsorption process contained by the catalyst for adsorb another molecule is adsorbent and another molecule that adsorbed is adsorbate. The adsorption process is caused by London Dispersion Forces, a type of Van der Waals Force which exists between molecules. The force acts in a similar way to gravitational forces between planets. London Dispersion

Forces are extremely short ranged and therefore sensitive to the distance between the adsorbent surface and the adsorbate molecule (Epling and Lin, 2002).

The electrostatic force is the attraction of the polar molecule between the polar-polar or non polar – non polar or polar-non polar molecule. Moreover, this force consist of many attraction characters for example; Orientation Effect, Dispersion Effect, Induction Effect.

The chemical force occur when the adsorbent react with adsorbate to produce new chemical compound such as the adsorption between functional group and transitional metal at the surface of the adsorbent by used electron together, barter electron or donated electron. Then, the attraction between the adsorbent's ions and the adsorbent's functional group will occur. This force is the irreversible.

2.2.2 Irradiation Process

The irradiation in the photocatalytic process uses ultraviolet light (UV) as a source of light for irradiation on the catalyst surface. Generally catalyst widely used in photocatalysis is semiconductors which have two band structures; the valence band, the high electric powers, and the conduction band which does not have electric power. See the Figure 2.2 below, when irradiated catalysts the electron transfers from valance band to conduction band. This can promote catalyst to have high productivity of electron donor or electron accepter with another ion in the solution.
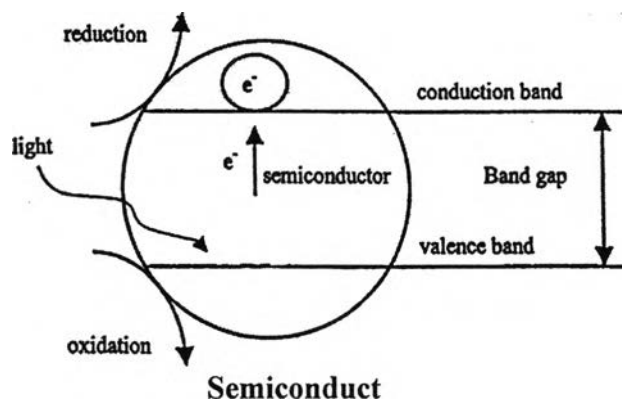

Figure 2.3 Reaction when irradiated catalysts (Fujishima, 1999)

The band gap between valance band and conduction band is specifically for each catalyst as showed in the Figure 2.3. The band gap is the important point in choosing the catalyst in photo reaction. Catalyst which has small band gap will not stable, electron from valence band can jump to conduction band and the recombination can occur. Other way, catalyst which has large band gap needs more energy for photocatalysis process.
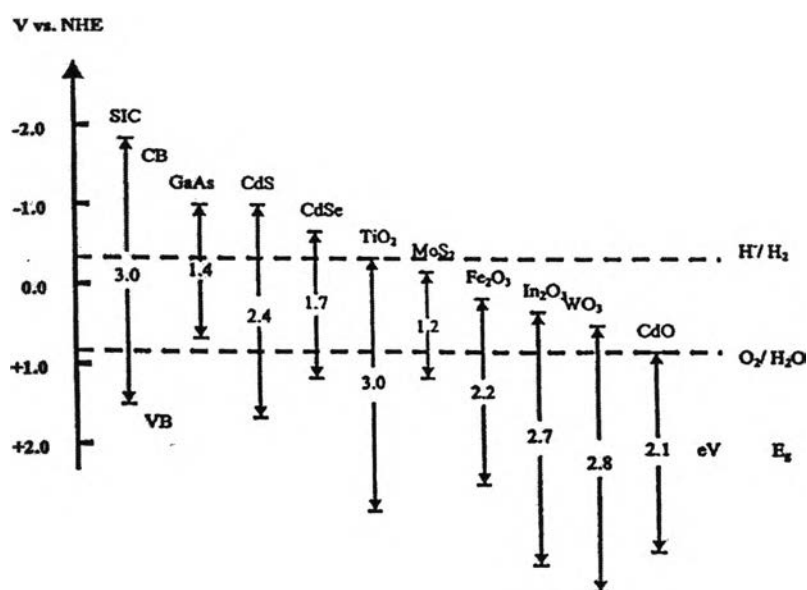

Figure 2.4 Band gap for each catalyst (Fujishima, 1999).

The qualification of TiO_2 is a neutral polar, when do not have excited state. The polar of TiO_2 depends on the environmental. For example, TiO_2 in the low pH solution (acidic solution) presents in positive polar. In contrast, TiO_2 in the high pH solution (basic solution) presents in negative polar. From this characteristic, TiO_2 is an alternative way for wastewater treatment especially in heavy metal and organic pollutant based on the redox reaction of photocatalytic process.
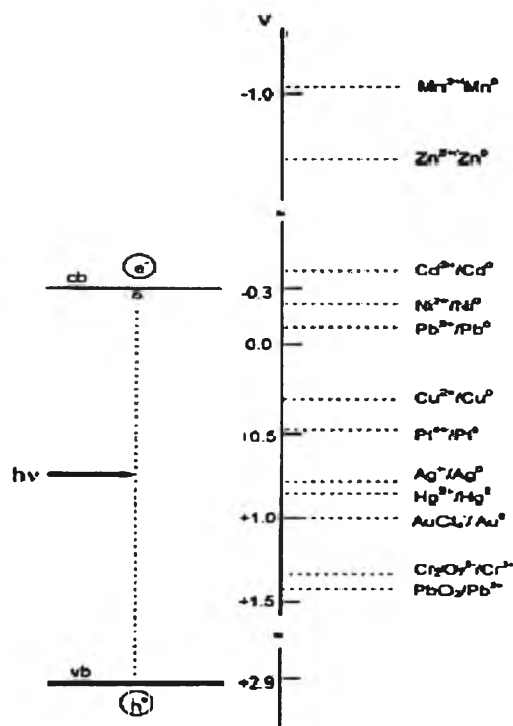
Figure 2.5 Reduction Potential of heavy metal and TiO_2 at pH 1 (Litter, 1999)

Photocatalytic process is well established by the irradiation of TiO_2 with light energy greater than the band gap energy of the semiconductor (hv>Eg =3.2 eV), conduction band electrons (e⁻) and valence band holes (h⁺) are generated. After this primary event, part of the photogenerated carricrs recombine in the bulk of the semiconductor with heat emission, while the rest reach the surface where the holes as well as the electrons act as powerful oxidants and reductants respectively. The photogenerated electrons react with the adsorbed molecular O_2 on the Ti (IV)-sites reducing it to superoxide radical anion $O_2^{\bullet-}$, while the photogenerated holes can oxidize either the pollute molecules directly or the OH⁻ ions and the H_2O molecules adsorbed at the TiO_2 surface to OH• radicals (Figure 2.4 (a)). These together with other highly oxidant species (peroxide radicals) are responsible for the primary oxidizing step in photocatalysis (Pelizzetti and Minero., 1993). According to this, the relevant steps of the photodegradation process at the semiconductor surface can be summarized by the reactions in Figure 2.4 (b). The OH• radicals formed on the illuminated semiconductor surface are very strong oxidizing agents with an oxidation potential of 2.8 V. These can easily attack the adsorbed pollute molecules or those

located close to the surface of the catalyst, thus finally leading to their complete mineralization. (Poulios et al., 1999)
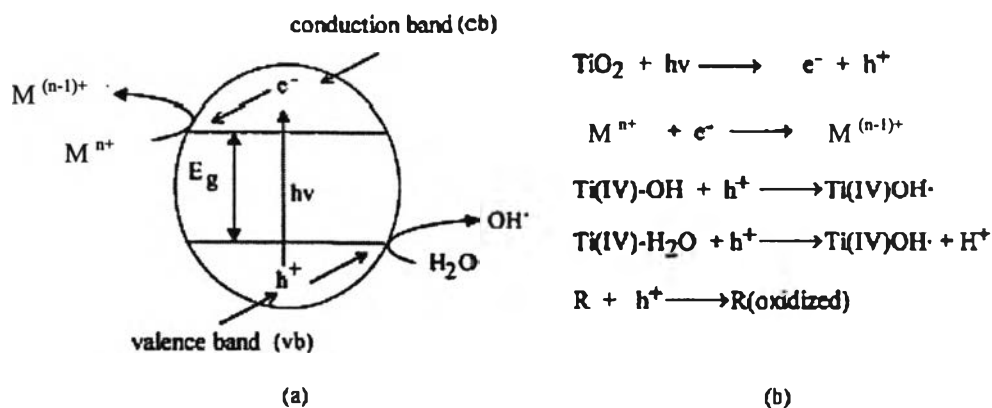
conduction band (cb)

$M^{(n-1)+}$

M^{n+}

E_g hv

OH·

H_2O

valence band (vb)

(a)

$$TiO_2 + hv \longrightarrow e^- + h^+$$

$$M^{n+} + e^- \longrightarrow M^{(n-1)+}$$

$$Ti(IV)\text{-}OH + h^+ \longrightarrow Ti(IV)OH\cdot$$

$$Ti(IV)\text{-}H_2O + h^+ \longrightarrow Ti(IV)OH\cdot + H^+$$

$$R + h^+ \longrightarrow R(oxidized)$$

(b)

Figure 2.6 (a) The TiO_2/solution interface under UV- illumination

(b) Reactions on the TiO_2 surface under UV-illumination

(Poulios et al., 1999)

2.3 Titanium Dioxide

Titanium is a common constituent of minerals, occurring in igneous rocks e.g., $BaTiO_3$, in silicates (olivines, pyroxenes), and iron-titanium oxides. Titanium dioxide (TiO_2) has been widely used in industry during the four last decades. The vast majority of its traditional applications exploit its very large dielectric constant and refractive index. Novel applications are instead based on its surface and catalytic properties.

TiO_2 is a catalyst which has been extensively studied due to its photocatalytic activity under UV radiation, moreover its high surface activity, insoluble in diluted acid, non-toxicity, nature friendly and corrosion stability. Under favorable conditions, a wide range of organic and inorganic compounds can be mineralized to mineral acids, carbon dioxide and water or transformed into harmless species (Weng et al., 1997;

Litter, 1999). TiO_2 appears in nature in three crystalline modifications, rutile (tetragonal), anatase (body centered tetragonal), and brookite (orthorhombic). Specifically in the form of anatase promote high activity in the photocatalyst. Upon increasing temperature, all polymorphs transform to rutile which is the most stable structure. In particular, anatase and brookite transform to rutile if heated to 700°C and 900°C, respectively. TiO_2 as used in the photocatalysis process always exists in two forms, one is the suspended form which is fine particles spread in aqueous solution, and the other is the immobilized form as in thin films. Although the suspended TiO_2 can be used without any preparation techniques, it is associated with the difficult problem of separation to eliminate the used TiO_2, turbidity effect and recycle the catalysts after use.

$a = 4.593 Å$
$c = 2.959 Å$

$Eg = 3.1 eV$
$\rho = 4.250 g/cm^3$
$\Delta G_f^0 = -212.6 kcal/mole$

$a = 3.784 Å$
$c = 9.515 Å$

$Eg = 3.3 eV$
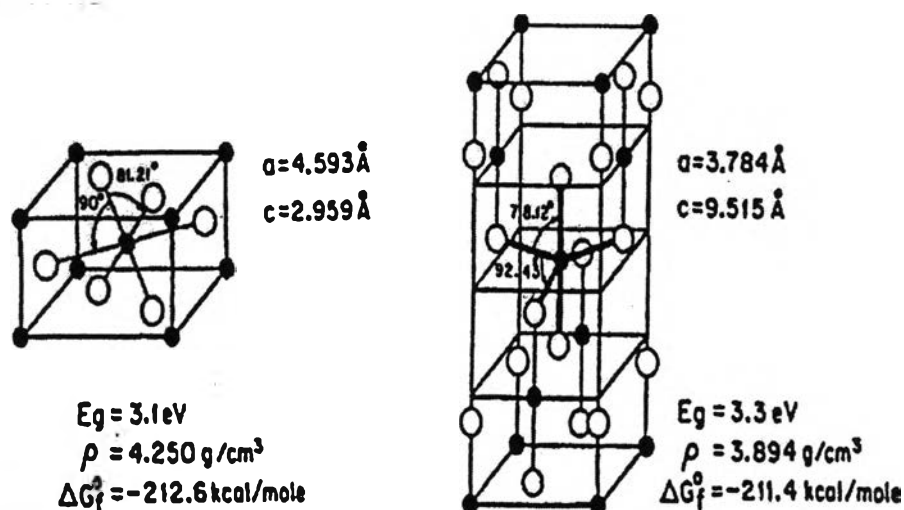$\rho = 3.894 g/cm^3$
$\Delta G_f^0 = -211.4 kcal/mole$

Figure 2.7 Conventional primitive cells of Rutile and Anatase. Black and white spheres represent titanium and oxygen atom, respectively (Linsebigler et. al., 1995)

Table 2.2 Property of Rutile and Anatase (Fujishima et al., 1999)

Property	Rutile	Anatase
Crystalline form	Orthorhombic	Orthorhombic
Band gab 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	1858°C	Changes to rutile at high temperature ~800°C

Application of Titanium Dioxide in water/wastewater treatment:

Weng et al. (1997) investigated the adsorption of chromium (VI) with TiO_2 as a catalyst. The results showed that the pH of solution was the key factor affecting the adsorption characteristics. The chromium (VI) adsorption was favorable under acidic conditions and the adsorbed ability is decreased when increasing pH and surface loading. Besides, decreasing temperature and ionic strength resulted in increasing adsorption capacity.

Matthews (1999) settle TiO_2 to a stationary support so as to avoid filtration and resuspension in a water purification process. In this research, 400 mg of TiO_2 was suspended in 80 cm^3 of water and then sucked into a borosilicate spiral glass tube. The end of the spiral was closed and vacuum applied while warm air was blown around the spiral. This process was repeated to produce a successive layer of TiO_2 on the inside surface of the tube. The effect of the amount of TiO_2 on the tube surface was studied by application of 50 µM of 500 cm^3 salicylic acid solution through the reactor at 120 cm^3 min^{-1}. In the presence of a 25 mg TiO_2 layer, an obvious decrease in concentration occurred with illumination time. Further increases in the thickness of the TiO_2 layer; 50 mg, 75 mg, 100 mg and 125 mg, resulted in an increase in the

decomposition rate but at a diminishing rate. Finally, it was reported that photooxidation of salicylic acid on TiO_2 films followed first–order kinetics.

Hilmi et al. (1999) used a glass plate coated with TiO_2 in a photocatalytic process to remove lead, copper, mercury and cadmium from an aqueous solution which containing individual metals and mixtures. TiO_2 was deposited on the glass plate from a suspension of TiO_2 (1.4 g/l). The titanium suspension (1 ml) was spread on one side of the glass and dried in 15 minutes on a hot plate at $100°C$. The coated glass pieces were cured for 2 hours in an oven at $400°C$. The results of metals removal demonstrated that 100 ml solution containing 10 ppm of each metal could be treated with a $10\ cm^2$ TiO_2-coated plate to leave an undetectable amount of metal in one hour.

Goeringer et al. (2001) found the synergism of photoreduction between two metal ions [copper (II) and chromium (VI)] beside UV irradiation of 2 g/l TiO_2. In the absence of copper (II), 800 µM chromium (VI) was not completely converted to chromium (III), even after 4 hours irradiation. While in the presence of 800µM copper (II) chromium (VI) reduction is completed within 20 minutes. In the same way, the half-life for the photoreduction of 600 µM copper (II) decreased from 1 hour with no chromium (VI) to 5 minutes in the presence of 1.6mM chromium (VI).

Schrank et al. (2002) studied the photocatalytic process by illuminate with UV light and used Titanium dioxide as a catalyst for remove chromium (VI) and dye with individual and mixture solution. In the individual solution, the result found that both chromium (VI) and dye were removed in acidic pH. In neutral pH, chromium (VI) can not remove because of chromium (VI) has low efficiency to adsorb on Titanium dioxide. Moreover, in the mixture condition (chromium mixed with dye), chromium have higher removal rate than in the individual solution since dye was oxidized by photo-excited holes which prevented electron-hole recombination and encouraged photoreduction of chromium (VI) on TiO_2. Another that, in the mixture condition dye

have higher removal rate than in the individual solution since the result of the prevention of electron-hole recombination by chromium (VI).

Watcharenwong (2003) investigated the removal of chromium (VI) from the synthesis wastewater by suspend TiO_2. The parameters emphasized are pH, concentration of chromium (VI) solution, amount of suspend TiO_2 and the effect of another ion which decrease photocatalytic activity. The results showed that, the optimum pH is 3 with 59.4% treatment efficiency. It was found that increasing the concentration of chromium (VI) can decrease K_{obs} value. The reaction rate of this research is pseudo-first-order. Adding of formate ion can increase the efficiency to 82.46%. However, in the other hand, another ions such as chloride, phosphate and sulphate can decrease photocatalytic activity.

Zhaolin and Liang (2004) investigated the benefit of Nano-TiO_2 thin film photocatalytic coating with illuminate wavelengths shorter than 385 nm. The resulting free-radicals and electron vacancies serve as very powerful oxidizing species that attack a variety of organic substances. TiO_2 thin film can anti-bacteria and anti-foiling surfaces and provide power suspensions for water and air purification systems, and powder packing for forming porous layers or filters that can be used as deodorizers.

Sobczyński et al. (2004) studied the mechanism of phenol photocatalytic decomposition and its intermediates in the presence of illuminated TiO_2. 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.

This thesis addressed the optimum conditions in treating chromium (VI) wastewater using photocatalytic reaction from the studied of Watcharenwong (2003). Then, the optimum condition in treating chromium (VI) from synthetic wastewater was used to find the operating parameters of RDPR in this work.

2.4 Sol-Gel process

The sol-gel process is a versatile technique for forming various amorphous materials, specifically ceramics and glasses (silica). This process is also accepted as a technology for forming thin films and coatings (Vossen and Kern, 1991). In general, the sol-gel process involves the transition of a system from a molecular precursor state through the formation of nano-sized bricks during the sol phase into a gel phase and finally transitions into a dried ceramic material. A sol is a colloidal (~1-1000 nm.) suspension of solid particles within a liquid phase. A gel is a substance which contains a porous three-dimensionally interconnected solid network throughout a liquid phase. The gel can be formed by polycondensation or by rapid evaporation of the solvent during film or fiber preparation to obtain xerogel, which is dried under normal conditions, and aerogel, which is dried under supercritical conditions such as in an autoclave (Brinker and Scherer, 1990).This derived materials as components for nanostructured energetic composite materials. Applying the sol-gel process, it is possible to fabricate ceramic or glass materials in a wide variety of forms: ultra-fine or spherical shaped powders, thin film coatings, ceramic fibers, microporous inorganic membranes, monolithic ceramics and glasses, or extremely porous aerogel materials. This methodology is used to make pyrotechnic materials with superior performance than existing formulations, while incorporating all the safety and low toxicity considerations of water or other environmentally acceptable processing solvent-based systems.

The sol-gel technique is the most widely used to prepare TiO_2 thin films because of its advantages: good homogeneity, large area coating and good photocatalytic properties (Klein, 1991). 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 and calcinations temperature (Arabatzia et al., 2002; Vicente et al., 2001; Yu et al., 2001).

Application of Sol-Gel method:

Pongpom (2005) synthesized thin film TiO_2 for chromium (VI) removal by photocatalysis process. In conclusion, the optimum condition for glass- TiO_2 thin film was in the condition ratio in titanium (IV) butoxide: ethanol: HCl: acetylacetone of 1: 30: 0.5: 1 as a calcinations temperature 500 °C and coating cycles of 3 films.

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

Ao et. al. (2003) developed the synthetic photocatalyst with TiO_2 by using the sol-gel method for photodegradation of typical indoor pollutants (CO, CO_2, NO_2, and water vapor) with direction to the commercial photocatalyst TiO_2 (P25). The synthetic photocatalyst was prepared from TTiP, ethanol and PEG600 in the molar ratio of TTiP: ethanol: PEG600 at 1:15:10. The catalyst was fixed on glass fiber by dip-coating. Subsequently, the glass fiber was dried at 100°C for 2 hours and then calcined at 450°C for 2 hours. The P25 catalyst was fixed on glass fiber by dipping it into a TiO_2 suspension and calcined at 120°C for 1 hour. The results showed that the synthetic photocatalyst had a higher activity than P25 for the degradation of NO, toluene, ethylbenzene, o-xylene (BTEX) and benzene.

Takahashi et al. (2001) investigated in synthetic of thin film TiO_2 by sol-gel method in the condition of titanium tetraisopropoxide (TTIP): ethanol: H_2O : HNO_3 as 1 : 1 : 10 : 1 and 1 : 1 : 50 : 1 with the difference dip-coating rates, which effect to the difference in thickness and amount of anatase crytal.

Douglas et al. (2001) prepared a thin film of TiO_2 by using the sol-gel method which dip coating and spin coating. The sol contained 5 grams of titanium tetraisopropoxide (TTIP), 40 mL of ethanol, 2.5 grams of PEG600 and 2.5grams of DEG. Thin films from dip-coated and spin-coated were calcined at $450^{\circ}C$ for 30 minutes in the furnace. The result present that, photocatalytic activities of both films were not different.

Arabatzis et al. (2002) generated TiO_2 thin films by applying dip coating and doctor-blade deposition techniques, using titanium (IV) butoxide and Degussa P25 TiO_2 powder as precursors. The results show that the Degussa P25 films presented very good uniformity crystallization, and properties closely related to the starting powder material. The catalytic activity of the films towards photodegradation of 3, 5-dichlorophenol was also analyzed. This works showed that the films could efficiently purely the pollutant. The reaction rate constants of the Degussa P25 films obtained from the doctor-blade technique were greater than the films obtained from the sol-gel technique.

Rookpun et al. (2003) investigated the optimum condition for the preparation thin films TiO_2. Titanium tetraisopropoxide (TTIP) and titanium dioxide (Degussa P25) were used as the precursors dissolved in ethanol. The provisional temperature was controlled at $0^{\circ}C$, the calcination (at $600^{\circ}C$) time was 20 minute and the solution was mixed for 30 minutes with 1 cycle of sol-gel coating process. The results showed that titanium tetraisopropoxide (TTIP) presented the physical properties for thin films

better than titanium dioxide (Degussa P25). The optimum conditions of titanium tetraisopropoxide (TTIP): ethanol: H_2O: HNO_3 as 1:50:1:0.2.

From the studied of Pongpom (2005), the results show the optimum conditions for produce thin film TiO_2 which can remove chromium (VI) by photoreduction. Therefore, the preparation of thin film TiO_2 rotating discs plates used in RDPR in this work was prepared following Pongpom's work.

2.5 Rotating Disc Photocatalytic Reactor (PRDR)

Reactor design can relieve some of the toxic pollutant's problems and this can increase the efficiency of the photocatalysis process. Many works incorporated the use of fixed films in order to reduce the need of filtration. Early in this decade, it was emphasized that in order to achieve commercialization of photocatalytic technology, many researchers in this field need to design photocatalytic reactors which can achieve higher efficiencies of light utilization and exhibit cost competitiveness when compared to other treatment technologies (Ollis et al. 1993).

Rotating Disc Photocatalytic Reactors (RDPR) have been used for several applications including the preparation of thin films, chemical synthesis, catalysis, and the dissolution of solids into solvents (Dionysiou et al., 1999). Recently, the rotating disc reactor incorporating TiO_2 catalyst and UV radiation was used for the photocatalytic degradation of toxic pollutants in the water.

The major advantages of RDPR

The major advantages of RDPR followed:

- By using immobilized TiO_2 in this reactor type, the post-treatment in separation of used catalyst from water is not required.

- This type of reactor provides high performance according to the photoreaction is occurring throughout the liquid thin film on the catalyst disc.

- This type of reactor reactor provides a good mixing of wastewater by the rotating of disc.

- Small size and ease to adjust the active surface area by adding thin film catalyst discs as required.

This thesis will be focused on the developed a novel photocatalytic reactor: the Rotating Disc Photocatalytic Reactor (RDPR). The degradation of toxic compounds can be carried out in continuous manner. Mixing of the solution was achieved by rotation of the discs while the photocatalytic reactions occured on the UV-irradiated composite TiO_2 based catalyst in the form of suspended was used as the immobilized photocatalyst on the rotating disc surface. This Rotating Disc Photocatalytic Reactor (RDPR) can be used for simultaneous degradation of toxic pollutant in both liquid and gas phases when the reactor is closed at the top (Hamill et al., 2000). It is anticipated that the process will be suitable for the degradation of chromium (VI) which do not lead them to purification using conventional adsorption (e.g., activated carbon adsorption) and oxidation (e.g., O_3) processes, as well as for disinfection (Jacoby et al., 1998). In a continuous mode of RDPR, the degradation rates of the pollutant can be controlled by many operating parameters including the illuminated surface area of the catalyst, the rotational speed of the disc, the liquid flow rate, the liquid carry capacity of discs and the level of the aqueous solution in the reaction vessel (Dionysiou et al., 2002). In this reactor, the removal of chromium (VI) can be carried out in continuous manner. The degradation rates of the chromium (VI) can be controlled by many operating parameters including initial pH of wastewater, the liquid flow rate and the rotational speed of the disc and the initial concentration of chromium (VI).

Application of Rotating Disc Photocatalytic Reactor (RDPR):

Dionysiou et al., (1999) studied in the destruction of 4-chlorobenzoic acid (4-CBA) by Rotating Disc Photocatalytic Reactor (RDPR) with immobilization of TiO_2 nanoparticles on the discs. The results show that, 288 μM of 4-CBA with pH 3 can be achieve removed in 6 hours beneath 365 nm of UV lamp and 4 rpm. The liquid carrying capacity of the catalyst discs will be increased when increase the disc angular velocity from 2-6 rpm, it's directly effect to increasing the reaction rate base on the photocatlysis reaction will occur only on the thin film catalyst. In this study Langmuir-Hinshelwood model was applied to investigate the reaction rate constant and the adsorption rate constant that equal to 12.5 $\mu mol/min$ and 7.0×10^{-3} $l/$ μmol. The mixing solution in this batch reactor was similar to an ideal continuously stirred tank reactor or CSTR (α and β are close to 1), which has the coefficients α and β of the equation (Westerterp et al., 1984): $C_{out}/C_0 = e^{\beta[-(t/\tau)]}$ are 1.03 and 0.98, respectively.

Hamill et al., (2000) studied the removal of a chlorinated VOC, 3,4-dichlorobut-1-ene by a batch rotating photocatalytic contactor with thin film of TiO_2. This paper studied the effect of dissolved oxygen concentration, light intensity and rotation speed on the degradation rate. The results show that the removal of VOC, 3, 4-dichlorobut-1-ene is the pseudo-first-order. The pseudo-first-order rate constants (k_{deg}) at the rotation speed of 5, 67 and 136 rpm are 0.0128, 0.0177 and 0.0242 min^{-1}, respectively. The dissolved oxygen concentration is not limiting in 0-100 rpm. When photon flux was increasing the photonic efficiency was reduced at all speeds, this is because of the increased electron-hole recombination rate at higher photon flux which results in the fractional order variation in light intensity.

Zhang (2000) studied the efficiency of rotating reactor (that is coated with TiO_2 powders and Pt are immobilized on outer surface of glass drum) for remove phenol and Total Organic Carbon (TOC) between the irradiation of solar light and artificial light. The result showed that artificial light has higher efficiency than solar

light in both contaminants. In both case, phenol has higher removal efficiency than TOC. This result is responding to the photocatalytic reaction which occurs in the appropriate wavelength (300-400 nm) depend on the chosen catalyst.

Dionysiou et al., (2002) investigated 3 parameters included the disc angular velocity, contaminant concentration and incident light intensity using a rotating disc photocatalytic reactor on the degradation of organic contaminants. The results showed that, high of disc angular velocity can promote the increase of photoreaction rate in 2-20 rpm. The increasing efficiency degradation rate responded to the intensity of light and the increasing of contaminant concentration. Moreover, the obtained results suggested the absence of significant mass transfer limitations at disc angular velocities higher than 6 rpm.

The knowledge from these papers was the basic principle of Rotating Disc Photocatalytic Reactors (RDPR) in small scale of batch reactor. The goals of these researches look forward for treatment of the toxic pollutant in the real industry wastewater.

2.6 Photocatalytic reaction.

2.6.1 Langmuir-Hinshelwood reaction kinetics

Langmuir-Hinshelwood kinetics (L-H) model is commomly used for quantitative description of heterogeneous phase reactions between two adsorbed reactants that take place on the interface of two systems (Fernandez et al., 1999). It has also been efficient as a standard quantitative description of liquid-solid reactions (Al-Ekabi et al., 1988). Extrapolation of L-H model for liquid-solid reactions requires some modification for TiO_2 solid surface in aqueous suspension, since hydroxyl groups and water molecules cover it.

The competitive analysis of the kinetic in the photocatalytic reduction of contaminants via irradiated semiconductors, TiO_2 distinguishes four situations:

1) The reaction take place between two adsorbed reagents;

2) The reaction occur between a redical in the solution and the adsorbed reagent;

3) The reaction take place between the radical linked to the surface and the reagents in the solution;

4) The reaction occurs with both species in the solution.

Therefore, for the standard L-H information, it is assumed that the reaction occurs on the surface of the substrate. In photocatalytic (or photoadsorption) reactions, the rate dependence on reagent concentration that can be approximated by the equation:

$$r = -\frac{dC}{dt} = \frac{kKC}{(1 + KC)} \qquad (2.1)$$

$$r = k_{obs}.C \qquad (2.2)$$

$$\frac{1}{k_{obs}} = \frac{C}{k} + \frac{1}{kK} \qquad (2.3)$$

Where r   is   the initial rate of disappearance of the contaminants, mg/l.min.

k is   an apparent reaction rate constants which is related to the adsorption/desorption affinity. It depends on light intensity, mg/l.min.

K is   the Langmuir constant reflecting the adsorption equilibrium between the reagent and the surface of the photocatalyst, l/mg.

C is   the reactant concentration, mg/l.

k_{obs} is   the reaction rate constant, min^{-1}.