

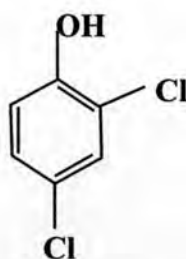


## CHAPTER II

### BACKGROUND AND LITERATURE REVIEW

#### 2.1 Chlorophenol (CPs)

CPs are chlorinated aromatic compounds which produced by adding chlorines to phenol. There are 5 basic types of CPs consist of monochlorophenols, dichlorophenols, trichlorophenols, tetrachlorophenols and pentachlorophenols (Agency for Toxic Substances and Disease Registry [ATSDR], 1999: online). Amongst the various types of CPs, 2,4-dichlorophenol (2,4-DCP) is the most important substance that should be observed, due to its highly toxicity and difficult to remove from wastewater. The basic structure of 2,4-DCP is shown in Figure 2.1 2,4-DCP is a white-crystalline solid at room temperature and a colorless liquid when molten. It has a strong phenolic odor and highly water-soluble. The 2,4-DCP information and its chemical and physical properties are listed in Table 2.1. (Ministry of Economy, Trade and Industry of Japan [METI], 2008: online and Dow AgroSciences, 2000: online).



**Figure 2.1** Structure formula of 2,4-DCP

2,4-DCP is a common pollutant in industrial wastewater. It is used as an important chemical intermediate in the production of pesticides and herbicides and pharmaceuticals. It is also used as a substrate to produce miticide or further chlorinated to pentachlorophenol in a wood preservative (Momani, Sans and Esplugas., 2003).

**Table 2.1** Information, chemical and physical properties of 2,4-DCP

<b>Substance name</b>	2,4-dichlorophenol
<b>CAS number</b>	120-83-2
<b>Molecular formula</b>	C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub> O
<b>Synonyms</b>	2,4-DCP; 2,4-Dichlorohydroxybenzene
<b>Molecular weight</b>	163 g
<b>Melting point</b>	45°C
<b>Boiling point</b>	215°C
<b>Density</b>	1.383 ppm at 25°C
<b>Water solubility</b>	4500 ppm at 25°C
<b>Log octanol-water partition coefficient</b>	7.68

Releases of 2,4-DCP may occur in effluents from its manufacture and use in the chemical industry. Small amounts may also be released from water treatment and wood pulp bleaching chlorination processes and from the degradation of various pesticides in soil.

The 2,4-DCP have been concerned on effect to human health, many kind of animal and aquatic life, due to the wide application of 2,4-DCP and its dreadful toxicity. It can disturb to human and animal's endocrine system (Bao, Xiang-zhong and Peng., 2007). Moreover, the risks of 2,4-DCP solution is devoted attention due to it is absorbed to the skin. It is immediately absorbed to the skin in amounts that have caused rapid death in human and direct contact can irritate the corneal, which could result in permanent impairment of vision (Dow AgroSciences, 2000: online). Furthermore, 2,4-DCP can causes a number of adverse health effects such as irritate the respiratory tract, kidneys, liver and blood-forming organs are known (Ormad, Ovelleiro and Kiwi., 2001). In addition, this chemical is very toxic to the single-celled eukaryotic organism, which is comparable in sensitiveness and responsiveness to human tissue cells (Greenpeace Research Laboratories., 2003: online).

According to EPA's complication of national recommended water quality criteria for the protection of aquatic life and human health in surface water, the recommended criteria for 2,4-DCP, in case of human health for the consumption of water and organism is 70 µg/L, and for the consumption of organism only is 290 µg/L (U.S. Environmental Protection Agency [U.S. EPA], 2008). The EPA recommends that for drinking water contain no more than 0.03 mg/L for a 1-day, 10-day, or longer exposure for a child (ATSDR, 1999). In the wastewater, the minimum quality objective is 20 µg/L (Estevinho et al., 2007). In Thailand, the Pollution Control Department (PCD) established a standard of industrial effluents for the phenol compounds to be no more than 1 mg/L (Pollution Control Department [PCD], 1996: online).

In Thailand, 2,4-DCP were detected especially in water samples collected from river and sea along the coastal area in the upper gulf of Thailand, this report is the result from the monitoring of endocrine disruptor compounds in the coastal hydrosphere of Thailand (Environmental Research and Training Center, 2001: online). In addition, the exploration of environmental pollutants in the Bangpoo industrial estate, Samut-Prakan province of Thailand showed widespread contamination in and around the area with a range of toxic and persistent organic pollutants including 2,4-DCP. The presence of organic contaminants in the treated water is a clear indication of the insufficient treatment of effluents, which leads to continuous pollution of the environment with persistent and toxic substances (Greenpeace Research Laboratories, 2003; online).

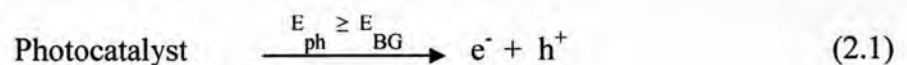
The conventional destructive method for 2,4-DCP have been different physical, chemical and biological methods, were used for removal of CPs from wastewater. Adsorption, precipitation, flocculation and ion exchange methods are usually used for remove the CPs on the solid phase, but not for complete mineralization, require a post-treatment to remove the pollutants from the new contaminated environment. Chemical or biological oxidation methods are used for complete mineralization of CPs. Biodegradation of CPs are more specific and relatively inexpensive, But it is difficult to remove CPs from wastewaters by conventional biological treatment

processes. Due to its toxic effects on activated sludge bacteria. (Kargi and Eker, 2004). In the recent year, advanced oxidation processes (AOPs) have been extensively utilized for the decomposition of hazardous or recalcitrant pollutants in the environment (Chang et al., 2009), and photocatalysis is the one of AOPs.

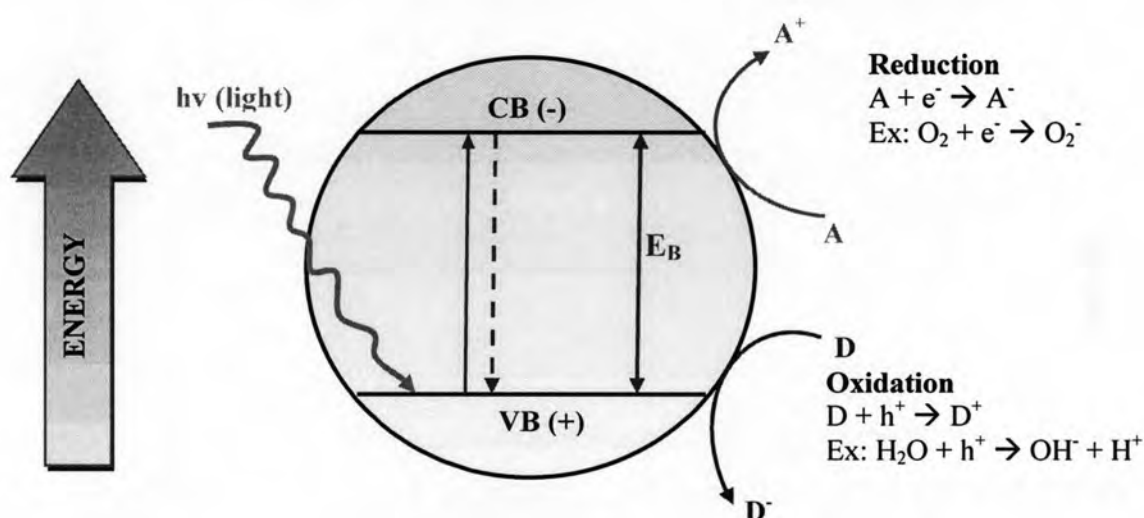
## 2.2 Basic Principles of Photocatalysis

Catalysis is the substrates which increase the rate of a chemical reaction. Normally, it is classified in 2 classes, first is homogeneous catalyst that show in the same phase with the reagent. The second is heterogeneous catalyst which act in a different phases with the reactants. Most heterogeneous catalysts are solids that act on substrates in a liquid or gaseous reaction mixture. Heterogeneous catalyst can be used in several fields such as synthesis of ammonia in Haber process and used as accelerant in photocatalysis.

Photocatalysis is the chemical reactions, which are stimulated by light and catalyst, which light in a wavelength range appropriate to stimulate into action the catalyst. The energy must be greater than or equal to the value within the band gap catalyst. It will enable the process. The basic principles of heterogeneous photocatalyst are described elsewhere by Litter (1999) as brief shortly, photocatalyst is a semiconductor (SC), which is characterized by an electronic band structure in which the highest occupied energy band, called valence band (VB), and the lowest empty band, called conduction band (CB), are separated by a bandgap energy, which is a region of forbidden energy in a particle. When a photon of energy higher or equal to the bandgap energy is absorbed by a semiconductor particle (Equation 2.1), an electron from the VB is promoted to the CB with simultaneous generation of a hole ( $h^+$ ) in the VB. The  $e_{CB}^-$  and the  $h_{VB}^+$  can recombine on the surface or in the bulk of the particle, the energy dissipated as heat or can be trapped in surface states where they can react with donor (D) or acceptor (A) species adsorbed or close to the surface of the particle. Thereby, subsequent anodic and cathodic redox reactions can be initiated (Figure 2.2).



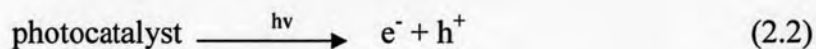
The energy level at the bottom of the CB is actually the reduction potential of photoelectrons and the energy level at the top of the VB determines the oxidizing ability of photoholes, each value reflecting the ability of the system to promote reductions and oxidations. The efficiency of a photocatalyst depends on the competition of different interface transfer processes involving electrons and holes and their deactivation by recombination.



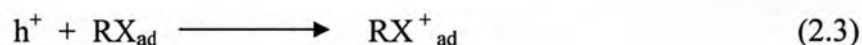
**Figure 2.2** Photocatalysis process on the surface of semiconductor particle.

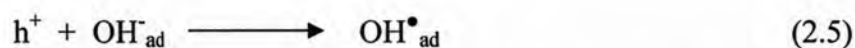
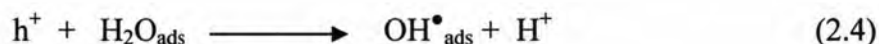
The photocatalytic process is a complex sequence of reactions that can be expressed by the following set of simplified equations (De Lasa et al., 2005):

A photocatalyst generates an electron and an electron-hole.

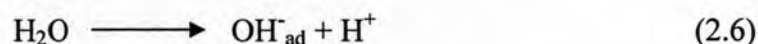


Electron transfer from the adsorbed substrate ( $RX_{ad}$ ), adsorbed water or the  $OH_{ad}$  ion, to the electron-hole.





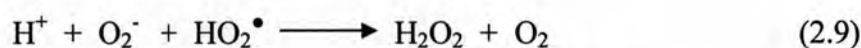
The importance step, because of the high concentrations of  $OH^-$ , given water dissociation into ions.



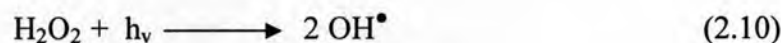
Molecular oxygen acts as an acceptor species in the electron-transfer reaction



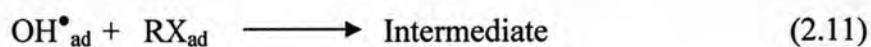
Super-oxide anions (Equation 2.7) can subsequently be involved in the following reaction.



Photoconversion of hydrogen peroxide gives more  $OH^{\bullet}$  free radical groups.



Finally,  $OH^{\bullet}$  radical oxidize organic adsorbed pollutants ( $RX_{ad}$ ) onto the surface of the  $TiO_2$  particles.



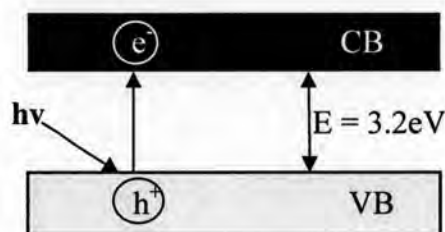
The  $OH^{\bullet}$  radicals, as described by Equation 2.11, are very reactive and attack the pollutant molecule to degrade it into mineral acid including carbon dioxide and water.

The direct oxidation via a surface-bond hydroxyl radical mechanism, there is an intermediate presence of hydroxylated structure during the photodegradation of halogenated aromatics. These hydroxylated intermediates are also found when similar aromatics react with a known source of hydroxyl radicals. Furthermore, ESR studies confirm the existence of hydroxyl and hydro-peroxy radicals in aqueous solutions of illuminated  $\text{TiO}_2$ .

### 2.2.1 Titanium dioxide ( $\text{TiO}_2$ ) as Photocatalyst

$\text{TiO}_2$  is excellent for photocatalytically breaking down organic compounds.  $\text{TiO}_2$  is close to the ideal catalyst in many respects for example, the availability of a material, inexpensive, highly stable and the photogenerated holes are highly oxidizing. Moreover, photogenerated electrons are reducing enough to produce superoxide from dioxygen (Fujishima, Rao and Tryk., 2000).

$\text{TiO}_2$  exists in two main crystallographic forms, anatase and rutile. The energy band gap of anatase is 3.23 eV (384 nm) and rutile is 3.02 eV (411 nm). Anatase photocatalytically more active than rutile (Litter, 1999).



**Figure 2.3** Energy band gap of  $\text{TiO}_2$

$\text{TiO}_2$  is a semiconductor which turns to a high-energy state by receiving light energy, and releases electrons from its illuminated surface (Figure 2.3). If the received energy at this stage is high enough, the electrons will jump up to conduction band. The energy is provided by light, and this light energy is believed to be the energy of the light's wavelengths. Therefore, a necessary wavelength is approximate 390 nm, which light needed to activate photocatalyst. This light should have the same

wavelength as ultraviolet light. Due to the large band gap of  $\text{TiO}_2$ , its practical application is inhibited for the low photon utilization efficiency and need only an ultraviolet source which accounts for only small fraction of the solar light (3-5%). Consequently, it is an important to develop new  $\text{TiO}_2$ -photocatalyst system with enhanced activities under both UV and visible light irradiation (200-700 nm) (Cong et al., 2007).

### **2.2.2 Surface modification of $\text{TiO}_2$ by using co-doping**

Doping process is a method to change the bare semiconductor to an impurity semiconductor by adding the impurity atom. Therefore, the electron and hole of bare semiconductor are changed.

Impurity doping is one of the methods to extend the spectral response of the  $\text{TiO}_2$  from ultraviolet to visible light region. In recent year, many researchers has been study by adding some metal elements such as Fe, Cr, Co, and V (Barakat et al., 2004; Zhou et al., 2005; Fana et al., 2008; EnGu, Yang and Hu., 2008) for tune the electronic structure and enhanced the photodegradation of the  $\text{TiO}_2$ . They have been found the advantages of the doping of the metal ion in  $\text{TiO}_2$  are the temporary trapping of the photogenerated charge carriers by the dopants and the inhibition of their recombination during migration from inside of the particle to the surface or the enhanced adsorption of the pollutants onto the doping ion surface sites. Moreover, many efforts have been attempted by modification  $\text{TiO}_2$  with nonmetals, such as B, N, and S. They have been investigated that anion doping of  $\text{TiO}_2$  has considerable effects on the band gap alteration. The success in nitrogen doping increase the photodegradation of  $\text{TiO}_2$  in visible light provides good opportunities for extensive applications such as oxidation of CO, ethanol, gaseous 2-propanol, acetaldehyde,  $\text{NO}_x$  and the decomposition of dyes such as methylene blue (Cong et al., 2007; Yu J. et al., 2006; Zhao et al., 2004). Nowadays, many methods are developed for  $\text{TiO}_2$  synthesis such as hydrothermal method, sonochemical method, solvothermal method and sol-gel method (Chen and Mao, 2007). In this work, sol-gel method will be used for catalyst synthesis.



### 2.2.3 Structure modification of TiO<sub>2</sub> by using template

TiO<sub>2</sub> is one of the metal oxides that suffer fast hydrolysis and condensation reaction resulting in poorly structured and even non-porous material. The mesoporous TiO<sub>2</sub> will be obtain by control over the hydrolysis and condensation reaction and other aspects will allow the formation of determined porous materials (Meynen, Cool and Vansant., 2009). The porous can increase the redox processes in photocatalysis by increase the surface area of photocatalyst (Yan et al., 2004). The correlation between the route parameters, the final surface and the structure properties demonstrate the important of controlling the synthesis processes. The best photocatalyst is presented well-crystallized anatase structure with low crystallite size, high surface area value and the cleanest surface (Colon et al., 2007). The basis of such method is the employment of organics with different types of functional groups such as hydroxyl, carboxylate and amine group, as a template for produce a desired product with the required shapes and interface structures of organic modifiers with crystal surface (Ryu Y. B. et al., 2007).

### 2.3 Sol-gel method

Sol-gel is the popular technique for preparing crystalline of TiO<sub>2</sub> because this technique control the structure of material on nanometer scale from the earliest stage of processing (Hench and West, 1990).

The sol-gel process involves the transition of a system from a liquid "sol" into a solid "gel" phase. An overview of the sol-gel process is presented in a simple work following. The starting materials used in the preparation of the "sol" are usually inorganic metal salts or metal organic compounds such as titanium (IV) alkoxides. In a typical sol-gel process, the titanium precursor is subjected to a series of hydrolysis and polymerization reactions to form a colloidal suspension, or a "sol". When the "sol" is casted into a mold, a wet "gel" will be formed. With further drying and heat-treatment, the "gel" is converted into TiO<sub>2</sub> (Chemat Technology, 1998: online). This method has much advantage for synthesis TiO<sub>2</sub> photocatalyst such as flexible control of pore structures and dopant concentration (Zhou et al., 2005).