

CHAPTER 2

Literature review

2.1 Photocatalysis of doped titanium dioxide

Photocatalysis is a well known advanced oxidation process (AOP) for the degradation of volatile organic pollutants at mild conditions. Industrial wastewater usually contains highly toxic pollutants such as chlorophenol (CP). UV radiation from sunlight is decomposed organic compounds by oxidation process. But It's few effective because toxic pollutants is higher more than oxidation process. Therefore, the process should be applied to high effective by photodegradation by TiO_2 photocatalys is and TiO_2 prepared by Hydrothermal method (Furukawa & Fujihara, 2008). Scanning electron microscope (SEM) was conducted to examine the morphology catalyst surface. The experiments were conducted with three types of TiO_2 – scientific grade powder (P25), commercial grade powder and commercial grade sand to find a cost effective solution to remove the contaminants like 2-chlorophenol (2-CP). The effect of water depth on the rate of degradation and parameters such as calcination temperature, amount of dopants, initial of pH and initial concentration were also studied. The organic compounds can be removed by ultraviolet (UV) radiation using oxidation process. The process can be accelerated by using a photocatalyst. However, the process is less effective cause large amount of toxic effluent entering the main stream water. Studies have shown that photocatalytic oxidation (PCO) with semiconductor like TiO_2 can be enhanced up to 50 times more than natural photo-oxidation (Farooq et al., 2009). According to studies, the processes have been studied extensively by numerous researchers and the experiments have been resulted optimum decontamination at ambient temperature (Wang et al. 2010). Titanium dioxide (TiO_2) is used for photocatalyst in water treatment systems. Because that it high efficiencies and TiO_2 has good spectral overlap with near UV radiation. Titanium dioxide (TiO_2) has band gap energy of 3.2 eV, equivalent to about 400 nm spectral energy (Wang et al., 2013). Therefore, TiO_2 is photoexcited by near UV radiation (300–400 nm range). Photocatalytic studies are primarily at the laboratory to lab scale phases of development.

Semiconductor photocatalysis with a primary focus on TiO₂ as a durable photocatalyst has been applied to a variety of problems of environmental interest in addition to water and air purification (Rafique et al., 2013). Because TiO₂ has proven to be the most suitable for wide spread environmental applications that, has ability to mineralize organic contaminants in wastewater to carbon dioxide and water. The reasons that TiO₂ has received so much research attention from stable nature toward photocorrosion, ease of preparation, non-toxicity, high ultraviolet absorptivity and strong oxidizing power toward great photochemical activity (D'Auria, 2011). The physical and chemical properties of the TiO₂ powder depend on the synthesis methods, selection of chemicals and addition of dopants among others. Variations in these factors lead to significant changes in TiO₂ structure, surface area phase composition, optical and electronic properties and most important the photocatalytic activity (Zainullina et al., 2015).

TiO₂ is biologically and chemically inert; it is stable with respect to photocorrosion and chemical corrosion and inexpensive. TiO₂ in the anatase form appears to be the most photoactivated the most practical of the semiconductors for widespread environmental application such as water purification, wastewater treatment, hazardous waste control, air purification, and water disinfection. In recent years, Degussa P25 TiO₂ has set the standard for photoreactivity in environmental applications Degussa P25 is a nonporous 70:30% anatase-to-rutile mixture with a Brunauer–Emmett–Teller (BET) surface area of $55 \pm 15 \text{ m}^2 \text{ g}^{-1}$ and crystallite sizes of 30 nm in 0.1 μm diameter aggregates. The application of illuminated semiconductors for the remediation of contaminants has been used successfully for a wide variety of compound such as alkanes, aliphatic alcohols, aliphatic carboxylic acids, alkenes, phenols, aromatic carboxylic acids, dyes, PCB's, simple aromatics, halogenated alkanes and alkenes, surfactants, and pesticides as well as for the reductive deposition of heavy metals (e.g., Pt⁴⁺, Au³⁺, Rh³⁺, Cr(VI)) from aqueous solution to surfaces. While photocatalyst titanium dioxide (TiO₂) absorbs Ultraviolet (UV) radiation from sunlight or illuminated light source (fluorescent lamps), it will produce pairs of electrons and holes. The electron of the valence band of titanium dioxide becomes excited when illuminated by light. The excess energy of this excited electron promoted the electron to the conduction band of titanium dioxide so that creating the negative-electron (e⁻) and positive-hole (h⁺) pair. This stage is referred as the semiconductor's 'photo-excitation' state. The energy difference between the valence band and the conduction band is known as the 'Band Gap'. Wavelength of the light necessary for photo-excitation is, $1240 \text{ (Planck's constant, } h) / 3.2 \text{ eV (band gap energy)}$ which is equal the wavelength energy of 388 nm.

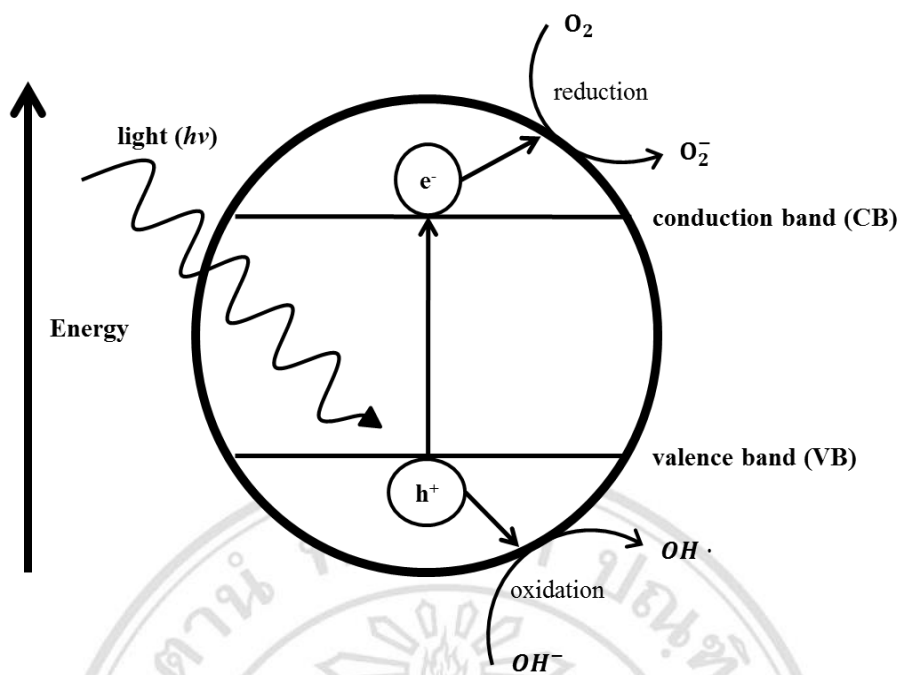


Figure 2.1 Reaction mechanisms (Herrmann et al., 2010)

The reaction mechanism of photocatalytic is shown in Figure 2.1. The positive-hole of titanium dioxide breaks apart the water molecule to form hydrogen gas and hydroxyl radical. The negative-electron reacts with oxygen molecule to form super oxide anion. This cycle continues when light is available.

It is generally accepted that the final electron traps are the species of the chemisorbed oxygen. They are produced from the transfer of photoexcited electrons to the oxygen molecules and can be described as O_2^- , O^- , and O_3^- . It has been suggested that the Ti^{4+} centers capture the photoexcited electrons, forming Ti^{3+} . The presence of surface defects which include oxygen vacancies and Ti^{3+} sites is known to be responsible for the chemisorption of molecular oxygen (Yang et al. 2000, Peral and Ollis 1992).

2.2 Photocatalysis of Titanium Dioxide with dopants

Doping of TiO_2 has many ways to synthesize, such as hydrothermal, precipitation nutrient compliance, sol – gel and impregnation. Hydrothermal method was used on this study. Doping of TiO_2 by hydrothermal process can be enhanced interfacial charge-transfer reactions of TiO_2 , doping of TiO_2 has been shown to increase the efficiency for the photocatalysis and inhibition of electron-hole recombination. The metal ion dopants in TiO_2 are listed in the Figure 2.2.

Photocatalytic Effects of Various Metal-Ion Dopants In Q-TiO₂

Li⁺ 0.15 <0.08												
			upper number Φ_{CHCl_3} (%)									
			lower number $\Phi_{\text{CCl}_4/\text{CHCl}_3}$ (%)									
Mg²⁺ 0.14 <0.08	V³⁺ 1.02 1.72		V⁵⁺ 0.51 0.66								Al³⁺ 0.08 <0.08	
Ti⁴⁺ 0.16 <0.08	V⁴⁺ 1.09 1.60	Cr³⁺ 0.21 0.16	Mn³⁺ 0.59 0.12	Fe³⁺ 2.38 1.74	Co³⁺ 0.08 <0.08	Ni²⁺ 0.50 0.09	Zn²⁺ 0.20 <0.08	Ga³⁺ 0.15 <0.08				
Zr⁴⁺ 0.09 0.11		Nb⁵⁺ 0.23 <0.08	Mo⁵⁺ 1.82 1.59		Ru³⁺ 1.72 0.38	Rh³⁺ 0.87 0.44				Sn⁴⁺ 0.11 <0.08	Sb⁵⁺ 0.15 <0.08	
		Ta⁵⁺ 0.27 <0.08		Re⁵⁺ 1.20 0.80		Os³⁺ 1.60 0.84						

Figure 2.2 Periodic chart of the photocatalysis effects of various metal ion dopants in TiO₂ (Michael R. Hoffmann et al., 1995)

Semiconductors (e.g., TiO₂, ZnO, Fe₂O₃, CdS, and ZnS) can be acted as sensitizers for light-reduced redox processes due to their electronic structure, which is characterized by a filled valence band and an empty conduction band. When a photon with an energy of $h\nu$ matches or exceeds the bandgap energy (E_g) of the semiconductor an electron is promoted from the valence band (VB) into the conduction band (CB) leaving a hole behind. Excited state conduction-band electrons and valence-band holes can be recombined and dissipated the input energy as heat, get trapped in metastable surface states, or react with electron donors and electron acceptors adsorbed on the semiconductor surface or within the surrounding electrical double layer of the charged particles. Several simple oxide and sulfide semiconductors have band-gap energy sufficiency for promoting or catalyzing a wide range of chemical reactions of environmental interest that show in table 2.1.

Table 2.1 Band gap of materials that can be the catalyst

Semiconductor	Band gap	Semiconductor	Band gap
Material	Energies (eV)	Material	Energies (eV)
Diamond	5.4	WO₃	2.76
CdS	2.42	Si	1.17
ZnS	3.6	Ge	0.744
ZnO	3.436	Fe₂O₃	2.3
TiO₂	3.03	PbS	0.286
CdS	2.582	PbSe	0.165
SnO₂	3.54	ZrO₂	3.87
CdSe	1.7	Cu₂O	2.172

Source: Thiruvengkatachari et al., 2008

The photocatalysis of the semiconductor started with photon absorption for which energy is equal or greater than to its band gap. Table 2.1 summarizes the common semiconductor materials with bandgap energies for which TiO₂ is superior among other catalysts (Farooq et al., 2009; Mozia et al., 2009). This process produces an electron-hole pair, the negative (e⁻) and positive (h⁺) that reacts with oxygen and H⁺ or OH⁻ in water to form •OH and •OH radicals (Zhang et. al., 2006; Li et. al., 2008; Thiruvengkatachari et. al., 2008; Shiraishi et al., 2009).

2.3 Hydrothermal method

The hydrothermal method is regarded as a convenient, inexpensive and environmentally innocuous method for producing high - quality TiO₂ nanotubes (Yu et al., 2003). Hydrothermal synthesis is a promising method because of the mild experimental conditions simple preparation process and lower cost (Li et al., 2015a). Firstly employed hydrothermal method to prepare oriented and single - crystalline rutile TNR films on FTO substrates for DSSC use. From then on, hydrothermal process was widely used to synthesize various TiO₂ with co-dopants. Hydrothermal synthesis is a relatively easy route to prepare highly-crystalline oxides under moderate reaction conditions. Hydrothermal media have been known to provide effective reaction environments for synthesize of nanocrystalline TiO₂ materials with high purities, homogeneous dispersions, and well-controlled crystallinities.

TiO₂ has three types of crystallographic structures: anatase, rutile, and brookite (He et al., 2013). Of those structures, anatase is known to hold the highest photocatalytic activity, despite its stability at ambient temperature. In addition, anatase crystals have low crystal lattice packing fractions and absorb more light than rutile crystals because of their reduced refractive indices. Rutile–anatase TiO₂ nanobranched arrays were prepared by hydrothermal methods. In general, hydrothermal synthesis is widely method to obtain nanocrystalline titanium particles, particle size and crystallinity could be controlled under high pressure. Moreover, it is a low temperature technique for materials development, widely applied in industrial processes for ceramic synthesis (Nikolić et al., 2011). The hydrothermal technique requires autoclave instrumentation and relies on the extensive heating of the nanoparticles diluted over an aqueous solution or slurry. It can control of the above factors by fine tuning of the autoclave parameters, which can lead to efficient immobilized titanium photocatalysts.

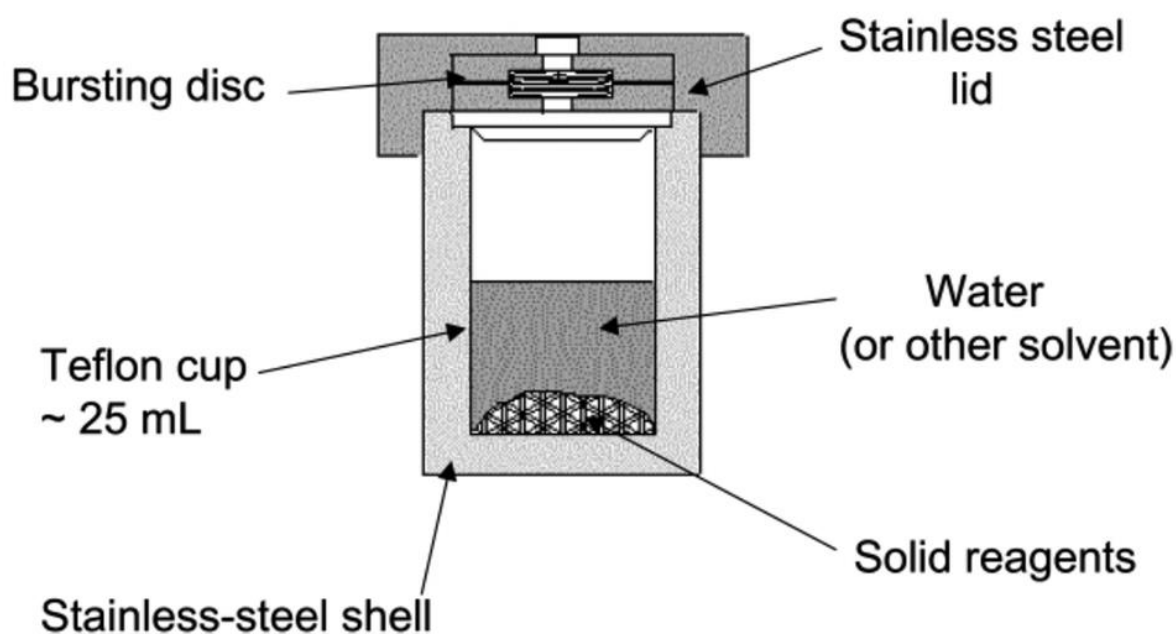


Figure 2.3 Hydrothermal synthesis reactor (Mari-Ann Einarsrud, *Chem. Soc. Rev.*, 2014)

Hydrothermal synthesis can be defined as a method of synthesis of single crystals which depends on the solubility of minerals in hot water under high pressure. The crystal growth is performed in an apparatus called “autoclave”. Possible advantages of the hydrothermal method over other types of crystal growth include the ability to create crystalline phases which are not stable at the melting point. Also, materials which have a high vapor pressure near their melting points can also be grown by the hydrothermal method. The method is also particularly suitable for the growth of large good-quality

crystals while maintaining good control over their composition. In general, hydrothermal synthesis is a prospective method to obtain nanocrystalline titanium particles, where polymorphism, particle size and crystallinity could be controlled under high pressure. Moreover, it is a low temperature technique for materials development, widely applied in industrial processes for ceramic synthesis. The hydrothermal technique requires autoclave instrumentation and relies

on the extensive heating of the nanoparticles diluted over an aqueous solution or slurry. The way to modification nanoparticle size and specific active area importantly affects the desired properties of the photocatalysts by varying the surface to volume ratio, by affecting the photo excited charge transfer and by influencing the surface hydroxyl concentration. The hydrothermal procedure of titanium powder at relatively low temperature ensures finely modification the properties of the modified titanium particles by only varying the duration of the treatment without the danger of the anatase phase transformation to rutile. Thus, optimum properties like increased roughness and complexity of the photocatalyst surfaces, and amplified hydroxyl content per unit area can be combined with improved interconnection of the nanoparticles and adhesion to the substrate. Control of the above factors by fine tuning of the autoclave parameters can lead to efficient immobilized titanium photocatalysts

2.4 Cerium

Cerium is the most abundant rare earth element that exhibits the ability to cycle between the Ce^{+3} (fully reduced) or Ce^{+4} (fully oxidized) state (Kumar et al., 2015). Cerium oxide (CeO_2) nanoparticles have been posited to exhibit potent anti-oxidant activity which may allow for the use of these materials in biomedical applications (Apel et al., 2012). The TiO_2 -Vanadium and TiO_2 -Cerium photocatalysts have higher visible light response with low particle size and high surface area. But TiO_2 -V showed better photocatalytic activity over 3,4 DCA with effective charge transfer than Ti-Ce (Padmini & Miranda, 2013). They used for doping with TiO_2 by hydrothermal calcination method. Therefore research of Synthesis and photocatalytic activity of mesoporous cerium doped TiO_2 as visible light sensitive photocatalyst can be concluded that the degradation could be achieved using visible light with both Ti-V and Ti-Ce as catalyst and also doping in the form of sol-gel instead of salts of the dopant lead to more efficient degradation(Šurca et al., 1999). They also used cerium doped TiO_2 were synthesized and varied the cerium concentration for 0 to 10 wt%. Present work shows that the cerium doping can stabilize the anatase phase. The photocatalytic activity is observed for cerium concentration having 5 wt%. Cerium doped

materials are Highest Remove and equally good Activity is found to depend on the presence of Ce^{4+} / Ce^{3+} rather than only visible light absorption. The results same like Cerium-doped titanium dioxide nano-powders were prepared through the sol-gel method using calcination temperature as $600^{\circ}C$ (Fan et al., 2006). The results of the photocatalytic experiments show that doping with Ce content of 0.08% - 0.4% can increase the photocatalytic activity of TiO_2 ; however, doping with Ce content of 0.5 % - 2.5 % can significantly decrease the photocatalytic activity of TiO_2 . The favorite doping content is 0.4% in the range of their experiments. Therefore an optimum amount of cerium with appropriate heat treatment is required so as to have best photocatalytic result under visible light.

2.5 Photocatalysis of 2-chlorophenol

Among the various organic wastes, chlorophenols are significantly harmful environmental pollutants due to their high toxicity, recalcitrance, bioaccumulation, and persistence in the environment (Abhilasha Dixit et al., 2011). Chlorophenols have been widely used as bactericides, insecticides, herbicides, fungicides and wood preservative as well as intermediates of dyes (Czaplicka & Kaczmarczyk, 2006). Chlorophenolic compounds are recalcitrant to biodegradation and persistent in the environment. They are considered harmful for human health due to their potential carcinogenic, mutagenic activity and toxicity. Unfortunately, chlorophenols are highly toxic and tend to persist in the environment that is why they have been listed as priority pollutants by the USEPA and the EU (P. Titus et al., 2004). Conventional processes to remove these pollutants involve physical, chemical and biological methods. Nevertheless, these techniques applied individually are generally limited and cannot degrade organic matter completely. The Some results of a laboratory-scale study of an environmentally friendly water treatment method was presented, where the organic model pollutant 2-chlorophenol (2-CP) was first adsorbed and then removed by a direct photolytic or heterogeneous photocatalytic process (Samir et al., 2005). The application of adsorption combined with direct photolysis and heterogeneous photocatalysis was studied, through the degradation of 2-chlorophenol, shorter-wavelength ($\geq 254nm$) and longer-wavelength ($\geq 310 nm$) irradiation were applied by another research.

A chlorophenol is any organochloride of phenol that contains one or more covalently bonded chlorine atoms. Chlorophenols are produced by electrophilic halogenation of phenol with chlorine. Most chlorophenols have a number of different isomers. Monochlorophenols have three isomers because there is one chlorine atom that can occupy one of three ring

positions on the phenol molecule; 2-chlorophenol, for example, is the isomer that has a chlorine atom in the ortho position. Pentachlorophenol, by contrast, has one isomer because all five available ring positions on the phenol are fully chlorinated. Chlorophenols are commonly used as pesticides, herbicides, and disinfectants. It is irritating and corrosive to the skin, eyes and mucous membranes. Physical and toxicity of chlorophenols are shown in table 2.2.

Table 2.2 MSDS of 2-chlorophenol

Property	Information
Name	2-chlorophenol / 2-hydroxychlorobenzene/ o-chlorophenol/ 1-chloro-2-hydroxybenzene, ochlorophenic acid, chlorophenolate
CAS number	95-57-8
Molecular formula	C ₆ H ₅ ClO
Molar mass	128.56 g/mol
Appearance	colorless to light brown liquid
Density	1.262 g/cm ³ , liquid
Melting point	8°C
Boiling point	173.0 - 175.0 °C
Flash point	63°C (closed cup)
Solubility in water	Slightly Soluble (20-25°C)
Vapor Density	4.4 (Air = 1)
Vapor Pressure	0.3 kPa (20°C)
Odor Threshold	1.24 ppm

The stability of the C-Cl bond in halo-hydrocarbons is responsible for their toxicity and persistence in the biological environment. The main entry routes of 2-chlorophenol to the aquatic environment are discharges from plants manufacturing it, or from plants, and those employ it as intermediate in the production of higher chlorinated phenols or phenoxy herbicides. Indirect sources were included discharges from paper mills as a by-product of chlorine-based bleaching, 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. 2-chlorophenol has very toxic and poorly biodegradable in water. A

wastewater stream containing 2-chlorophenol over 200 mg/l may not be treated effectively by direct biological methods.

There are many research studied on the oxidation of 2-chlorophenol under photocatalytic, electrocatalytic and Fenton's oxidation under various conditions to determine the influence of pH and the formation of oxidation intermediates and products. It has been observed that the types and distribution of intermediates was depending largely on the oxidation process and experimental conditions. Catechol and cyclopentadienic acids were reported to be the major intermediates from the degradation of 2-chlorophenol by photolysis whereas phenol, hydroquinone, benzoquinone, chlorohydroquinone and hydroxyl hydroquinone were identified.

However, sometimes, the toxicity of chlorophenols have too much for removed by UV radiation. So we use titanium dioxides (TiO_2) for Photocatalysis reaction. The intermediates produced during their degradation compromises the ability of these methods to completely mineralize in the wastewater. Latest investigations on the degradation of organic pollutants are focused on the combination of biological and physical-chemical treatments. This saves a considerable amount of energy in comparison with what is needed to achieve the full mineralization of the pollutants by chemical oxidation (Christoforidis et al., 2012).

Literture reported the degradation of generated chlorophenols from bleaching process during paper production by sequential biological-AOP using UV/ TiO_2 /RuxSey obtaining a 99% chlorophenols removal after 96 hour and 20 min with a 97% reduction in chemical oxygen demand (Pedroza et al., 2007). Moreover, another researchers evaluated the degradation of a mixture of chlorophenols by sequential AOP-biological process using activated sludge and either UV, UV/ TiO_2 / H_2O_2 , UV/ TiO_2 or UV/ H_2O_2 as oxidant agent (Samir et al., 2005)

2.6 Photocatalytic kinetic reaction

Photocatalysis is a process wherein the initial step encountered during the process is adsorption and followed by the photochemical reaction. Consider the following chemical reaction equation for a non-dissociative (molecular) adsorption process of chlorinated organic (chlorophenols) pollutant with the catalyst such as TiO_2 :



Where:

A, represents a vacant site (catalyst)

B, molecule (gas or liquid phase)

C, adsorption complex

If we assumed that the adsorption process is limited for a monolayer, it can be expressed using Langmuir equation such that there are fixed number of localized surface sites present on the surface. Defining an equilibrium constant (b) in terms of the concentration of the reactants and products shown in the following equation,

$$b = \frac{[C]}{[A][B]} \quad (\text{eq.2-2})$$

Changing $[C]$, $[A]$, and $[B]$ to q , $(1-q)$ and C , respectively, the above equation will be,

$$b = \frac{q}{(1-q)C} \quad (\text{eq.2-3})$$

Rearranging and solving for the surface coverage (q) for the organic compound gives the following expressions that is the usual form of Langmuir equation (Kim et al., 2008),

$$q = \frac{bC}{1+bC} \quad (\text{eq.2-4})$$

If consider the two process, adsorption-desorption where equilibrium exists between the catalyst and organic compound adsorbed in the surface of the catalyst, the following equation is considered.

$$q = \frac{q_m b C}{(b C + 1)} \quad (\text{eq.2-5})$$

Where:

b is the Langmuir constant related to the affinity of the binding sites

q is the amount of adsorbed material at equilibrium

q_m is the maximum adsorption capacity reflecting adsorption-desorption equilibrium

C is the concentration of organic compound in solution

Since the study focused on the TiO_2 with metal and non- metal dopant as adsorbent material, the following Freundlich equation was expressed.

$$q = KC^{\frac{1}{n}} \quad (\text{eq.2-6})$$

Where:

K is the Freundlich adsorption constant reflecting the adsorption capacity

n is the adsorption parameter

2.6.1 Langmuir-Hinshelwood expression

In the last decade, the mechanism of heterogeneous photocatalysis has been investigated by many researchers. A photocatalytic reaction proceeds on the surface of semiconductors have several steps: (i) production of electron-hole pairs by irradiating the semiconductor with light having an energy content higher than the band gap energy of the semiconductor; (ii) separation of the photogenerated electrons and holes due to trapping by species that are adsorbed on the semiconductor; (iii) redox reactions between the trapped electrons and holes and the adsorbents; (iv) desorption of reaction products and reconstruction of the surface .

The TiO_2 photocatalytic are a heterogeneous reactions, and the oxidation reaction can be achieved by hydroxyl radicals ($\bullet\text{OH}$) that clearly expressed by The Langmuir Hinshelwood model.

$$r = \frac{kKC}{1+KC} \quad (\text{eq.2-7})$$

In order to, the coefficients can be estimated the linearity equation of the Langmuire Hinshelwood model would be expressed.

$$\frac{1}{r} = \frac{1}{k} + \frac{1}{kKC} \quad (\text{eq.2-8})$$

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, K is the Langmuir constant reflecting the adsorption/desorption equilibrium between the pollutant and the surface of the photocatalyst, and C is the concentration of the pollutant.

2.6.2 Langmuir adsorption isotherm

Langmuir adsorption isotherm was developed by Irving Langmuir in 1916 to describe the dependence of the surface coverage of an adsorbed gas on the pressure of the gas above the surface at a fixed temperature. The basic idea behind the Langmuir model is the coverage of the surface by a monomolecular layer. The Langmuir adsorption isotherm was developed by assuming:

1. A fix number of accessible sites are available on the adsorbent surface, all which have the same energy.
2. Adsorption is reversible and monolayer or unilayer. Equilibrium is reached when the rate of adsorption of molecule onto the surface is the same as the rate of desorption of molecule from the surface. The rate at which of adsorption proceeds is proportional to the driving force, which is the difference between the amount of adsorbed at a particular concentration and the amount that can be adsorbed at that concentration. At the equilibrium concentration, this difference is zero.

Langmuir adsorption isotherm can be written as Equation (eq. 2-9):

$$q_e = \frac{q_{max}bC}{bC + 1} \quad (\text{eq.2-9})$$

Where; “ q_e ” represents moles of adsorbate per unit weight of adsorbent, “ b ” is rate constant ratio between adsorption and desorption, “ q_{max} ” is maximum moles of adsorbate per unit weight of adsorbent, and “ C ” is adsorbate aqueous concentration. This Equation is a linear line when plotted inverse q_{max} and inverse concentration rewritten as Equation (eq. 2-10):

$$\frac{1}{q_e} = \frac{1}{q_{max}b} \left(\frac{1}{C} \right) + \left(\frac{1}{q_{max}} \right) \quad (\text{eq.2-10})$$

2.7 The different studies on treatment of 2- chlorophenol by photocatalytic oxidation process using TiO₂ as catalyst

The photocatalytic activity of the synthesized TiO₂ photocatalyst in terms of 2-chlorophenol degradation efficiency is also compared to those reported from other studies. These studies are summarized in Table 2.3. The photocatalysts illuminated with ultraviolet light has shown higher photocatalytic activity when compared to photocatalysts illuminated with visible light. This is expected since the UV light has higher photon energy, and thus, it can generate more electron-hole pairs as compared to the visible light. When compared to the photocatalysts illuminated with visible light. TiO₂ with dopants and the photocatalyst synthesized. Generally, the study was focused on the performance as dopant in oxidation of 2-chlorophenol. There are different studies on treatment of chlorophenols by photocatalytic oxidation process using TiO₂ as catalyst which is related to the study and summarized in Table 2.3.

Table 2.3 Previous studies on the photocatalytic degradation of 2- chlorophenol

Title	Photocatalyst	Preparation of the catalyst	Light used	Degradation rate	Author(s) Publication
Size dependency of nanocrystalline TiO ₂ on its optical property and photocatalytic reactivity exemplified by 2-chlorophenol	TiO ₂	Metal–organic chemical vapor deposition	UV-Vis	100% in 180 min	(Lin et al., 2006)
Photocatalytic degradation of 2-chlorophenol by Co-doped TiO ₂ nanoparticles	Co-doped TiO ₂	Sol-gel method	UV-Vis	93.4% in 180 min	(Barakat et al., 2005)
The effect of the composition of tri-elemental doping (K, Al, S) on the photocatalytic performance of synthesized TiO ₂ nanoparticles in oxidizing 2-chlorophenol over visible light illumination	tri-elemental doping (K, Al, S) TiO ₂	Sol-gel method	Visible light	96% in 240 min	(Tolosa et al., 2011)

Table 2.3 Previous studies on the photocatalytic degradation of 2- chlorophenol (Con't)

Removal of 2-chlorophenol from water by adsorption combined with TiO ₂ photocatalysis	TiO ₂ Degussa	-	UV-Vis	99% in 90 min	(Ilisz et al., 2002)
Photocatalytic decomposition of 2-chlorophenol in aqueous solution by UV/TiO ₂ process with applied external bias voltage	TiO ₂ Degussa	-	UV-Vis	53% in 300 min	(Ku et al., 2006)
Preparation of nanostructured ruthenium doped titania for the photocatalytic degradation of 2-chlorophenol under visible light	Ru doped TiO ₂	Impregnation method	Visible light	61% in 60 min	(Elsalamony & Mahmoud)
Reaction paths and efficiency of photocatalysis on TiO ₂ and of H ₂ O ₂ photolysis in the degradation of 2-chlorophenol	TiO ₂ Degussa	-	UV-Vis	90% in 360 min	(Bertelli & Selli, 2006)

Table 2.3 Previous studies on the photocatalytic degradation of 2- chlorophenol (Con't)

Electrophoreted Zn-TiO ₂ -ZnO nanocomposite coating films for photocatalytic degradation of 2-chlorophenol	TiO ₂ -ZnO	Hydrothermal method	UV-Vis	97.3% in 180 min	(Abdel Aal et al., 2008)
TiO ₂ -In ₂ O ₃ photocatalysts: preparation, characterisations and activity for 2-chlorophenol degradation in water	TiO ₂ -In ₂ O ₃	Sol-gel method	UV-Vis	27% in 90min	(Shchukin et al., 2004)
Gallium- and iodine-co-doped titanium dioxide for photocatalytic degradation of 2-chlorophenol in aqueous solution: Role of gallium	Ga,I-TiO ₂	Sol-gel method	UV-Vis	90% in 240 min	(Fitzsimmons & Mausner, 2015)

Table 2.3 Previous studies on the photocatalytic degradation of 2- chlorophenol (Con't)

Degradation of 2-chlorophenol using carbon nanotube/titanium oxide composite prepared by hydrothermal method	carbon nanotube TiO ₂	Hydrothermal method	UV-Vis	75% in 240 min	(Juang et al., 2013)
2-Chlorophenol degradation via photo Fenton reaction employing zero valent iron nanoparticles	(ZVI) nanoparticles	-	UV-Vis	78% in 180 min	(Ortiz de la Plata et al., 2012)
Promoting effect of EDTA on catalytic activity of highly stable Al-Ni bimetal alloy for dechlorination of 2-chlorophenol	Al-Ni alloy particles	-	UV-Vis	99% in 90 min	(Yang et al., 2014)
The influence of pH and cadmium sulfide on the photocatalytic degradation of 2-chlorophenol in titanium dioxide suspensions	TiO ₂ mixed CdS	-	UV-Vis	99% in 60 min	(Doong et al., 2001)

Table 2.3 Previous studies on the photocatalytic degradation of 2- chlorophenol (Con't)

Synthesis of titanium dioxide nanoparticles using hdrothermal for degradation of chlorophenols	TiO ₂ /Ce	Hydrothermal method	Visible light	100% in 240 min	Current Study
Increasing the catalytic activities of iodine doped titanium dioxide by modifying with tin dioxide for the photodegradation of 2-chlorophenol under visible light irradiation	iodine doped TiO ₂	Hydrolysis method	UV-Vis	88% in 240 min	(He et al., 2011)