CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Photocatalysts

Various types of photocatalyst have been investigated as a potential catalyst to degrade organic matters. Titania and zinc oxide, which are inexpensive and non-toxic, becomes attractive for this research.

2.1.1 Physical and chemical properties of titania

Titanium dioxide is known as titanium (IV) oxide or titania, has great potential for many industrial applications. Titania has been used in many fields of application such as catalyst, catalyst support, electronics, cosmetic pigment and filter coating. In recent years, main attention has been devoted to its photocatalytic activity and photoinduced superhydrophilicity. Since titania has relatively wide band gap (3.2 eV), charge carriers, i.e. electrons and holes, are produced when titania is excited. Consequently, highly reactive radicals are generated and oxidation-reduction reaction of species adsorbed on the surface of titania can occur. The use of titania in the photocatalytic degradation of organic pollutants has attracted much attention as a promising method of depolluting contaminated waters and soils [11].

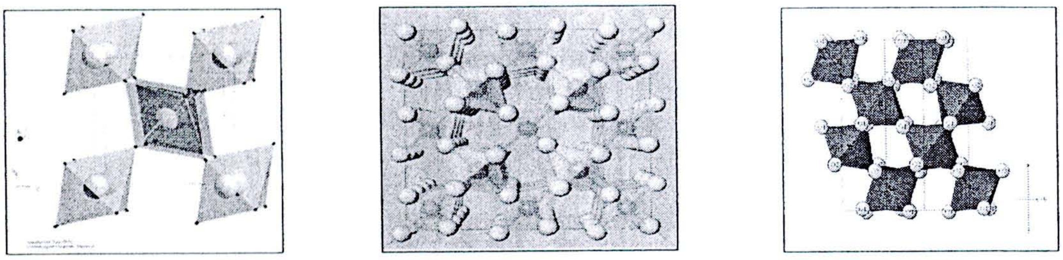
Titania occurs in nature as well-known minerals rutile, anatase and brookite, and additionally as two high pressure forms, a monoclinic baddeleyite-like form and an orthorhombic α-PbO_2-like form. The most common form is rutile, which is also the most stable form. Anatase and brookite can both convert to rutile upon heating. Anatase is a metastable phase, which tends to be more stable at low temperature. For brookite, it is formed under hydrothermal conditions and usually found only in mineral. Brookite has been produced by heating amorphous titania, which is prepared from the reaction between alkyl titanates with sodium or potassium hydroxide in an autoclave at 200 to 600°C. Although titania is known to have three natural polymorphs, only anatase is generally accepted to have significant photocatalytic activity [6].

The crystallographic characteristic of these varieties are shown in Table 2.1. Although anatase and rutile are both tetragonal, they are not isomorphous as shown in Figure 2.1. Anatase usually occurs in near-regular octahedral form, while rutile forms slender prismatic crystals that are frequently twinned. Nevertheless, both anatase and rutile are anisotropic of which physical properties vary according to direction relative to the crystal axes. However, in most applications using these substances, the distinction between crystallographic directions is lost because of the random orientation from large number of small particles or grains in the particle.

Table 2.1 Cystallographic characteristic of anatase, brookite and rutile.

Properties	**Anatase**	**Brookite**	**Rutile**
Crystal Structure	Tetragonal	Orthorhombic	Tetragonal
Optical	Uniaxial	Biaxial	Uniaxial
Density, g/cm^3	3.9	4.0	4.23
Lattice parameter, nm			
a	0.3758	0.9166	0.4584
b		0.5436	
c	0.9514	0.5135	2.953

Three allotropic forms of titania have been prepared artificially, but only rutile has been obtained in the form of transparent large single crystal. The transformation from anatase to rutile is accompanied by evolution of ca. 12.6 kJ/mol (3.01 kcal/mol). The rate of phase transformation is greatly affected by temperature and by presence of other substances which may either catalyze or inhibit the transformation. The lowest temperature at which the conversion from anatase to rutile takes place at a measurable rate is approximately 500-550°C [12]. The change is not reversible and it has been shown that ΔG for the transformation from anatase to rutile is always negative.



(a) (b) (c)

Figure 2.1 Crystal structure of TiO_2; (a) Rutile, (b) Anatase, (c) Brookite.

2.1.2 Physical and chemical properties of zinc oxide

Zinc oxide is an inorganic compound with the formula ZnO. Zinc oxide is a white or yellowish powder. It occurs in nature as the mineral zincite. It is nearly insoluble in water or alcohol, but it is soluble in acids and alkalies. Zinc oxide particles may be spherical, acicular or nodular depending on the manufacturing process. The particle shape is important for maximizing physical properties. Zinc oxide absorbs all UV light radiation at wavelength below 360 nm. Zinc oxide has received considerable attention because of its unique optical, semiconducting, piezoelectric, and magnetic properties. ZnO nanostructures exhibit interesting properties including high catalytic efficiency and strong adsorption ability. ZnO is able to degrade a wide range of recalcitrant organic and inorganic pollutants due to its ability to generate highly oxidizing and reducing species. It could be photo-excited by absorbing light of suitable wavelength to generate two types of electronic carriers, i.e. electrons (e^-; the reducing species) and holes (h^+; the oxidizing species).

Zinc oxide is an n-type semiconductor with a band gap of 3.20 eV and the free excitation energy of 60 meV, which makes it very high potential for room temperature light emission. This also gives zinc oxide strong resistance to high temperature electronic degradation during operation. Therefore, it is attractive for many opto-electronic applications in the range of blue and violet light as well as UV devices for wide range of technological applications. Zinc oxide also exhibits dual semiconducting and piezoelectric properties. A summary of the physical and chemical properties of zinc oxide are given in Table 2.2.

Table 2.2 Physical and chemical properties of zinc oxide.

Molecular formula	ZnO
Molecular weight	81.38 g/mole
Crystal structure	Hexagonal wurtzite Cubic zincblende Cubic rocksalt (The hexagonal wurtzite structure is most stable at ambient conditions and thus most common.)
Lattice parameters of hexagonal wurtzite at 300 K	
a	0.32495 nm
c	0.52069 nm
c/a	1.602 (ideal hexagonal structure is 1.633)
Density	5.606 g/cm^3
Melting point	1970 – 1975 °C (decomposes)
Energy gap	3.2 eV, direct
Excitation binding energy	60 meV
Appearance	White solid
Synonyms	Zinc white; Zinc flowers; Calamine; C.I. pigment white 4
Solubility	Insoluble in water and alcohols. Soluble in acids and bases.
Physicochemical stability	Stable under normal conditions of handling and storage.

Zinc oxide is a II-VI compound semiconductor of which the ionicity resides at the borderline between covalent and ionic semiconductor. The crystal structures shared by zinc oxide are wurtzite, zinc blende, and rocksalt, as schematically shown in Figure 2.2. At ambient conditions, the thermodynamically stable phase is wurtzite. The zinc-blende structure can be formed only by the growth of ZnO on cubic substrate. The rocksalt structure may be obtained at relatively high pressure.

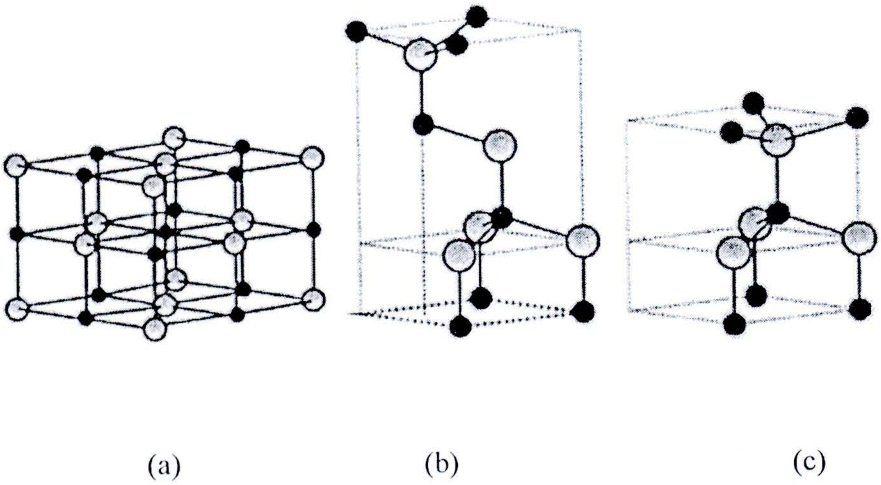


Figure 2.2 Stick and ball representation of zinc oxide crystal structures: **(a)** cubic rocksalt, (b) cubic zinc blende, and (c) hexagonal wurtzite. The shaded gray and black spheres denote Zn and O atoms, respectively.

Zinc oxide occurs in nature as mineral. Zinc oxide is prepared in industrial scale by vaporizing zinc metal and oxidizing the generated zinc vapor with preheated air. Zinc oxide has numerous industrial applications. It is a common white pigment in paints. It is used to make enamel, white printing ink, white glue, opaque glasses, and floor tiles. It is also used in cosmetics, pharmaceutical applications such as antiseptic and astringent, dental cements, batteries, electrical equipments, and piezoelectric devices. Other applications are the use as flame retardant, and UV absorber in plastics. Nevertheless, the current major application of zinc oxide is in the preparation of most zinc salts.

Gouvea et al. have reported that the activity of nanosized zinc oxide is higher than nanosized titania [13]. The smaller particle, the higher the photocatalytic activity and the coupling of titania with zinc oxide seems useful in order to achieve more efficient electron-hole pair separation under illumination and, consequently, a higher reaction rate.The increase in the lifetime of the photoproduced pairs, due to hole and electron transfer between the two coupled semiconductors, is produced in many cases as key factor for the improvement of the photoactivity [14].

2.1.3 Photocatalyst synthesis

There are several methods that can be used to synthesize photocatalyst. In general, methods which have been reported for titania and zinc oxide are: sol-gel method [5, 15], hydrothermal or solvothermal method [16, 17], and precipitation method [18, 19]. Previous researches have revealed that different photocatalyst synthesis methods result in different surface properties, which consequently affect the interaction between catalyst surface and the compound to be degraded. One of the popular techniques is sol-gel method because of its low cost, reliability, and simplicity. Sol-gel process is a route generally applied to prepare nanomaterial with notable advantages of high purity and good mocrostructure. So this method was selected to prepare photocatalyst in this work.

Sol-gel technology is quite important for processing materials [20]. This method can be performed at relatively low temperature to prepare a solid. Sol is firstly prepared from suitable reactants in suitable liquid. Sol preparation can be either simply the dispersion of insoluble solids in liquid or addition of precursor which reacts with the solvent to form a colloidal product. A typical example of the former approach is the dispersion of oxides or hydroxides in water with the pH adjusted so that the solid particles remain in suspension rather than precipitate out. A typical example of the later approach is the addition of metal alkoxide to water. The alkoxides are hydrolyzed giving the oxide as a colloidal product. The sol is then either treated or simply left to form gel. To obtain a final product, the gel is heated. This heating serves several purposes. It removes the solvent, decomposes anions such as alkoxides or carbonates to give oxides, allows rearrangement of the structure of the solid and allows crystallization. For the synthesis of titania, the process starts with the mixing of titanium alkoxide with alcohol. Acidic aqueous solution is subsequently added to the mixture [21]. Su et al. revealed that, the titania particles in the initial sol were elliptical in shape. The crystal size of titania increased from 4 to 35 nm as the temperature of the calcination was increased to 700 °C. The specific surface area decreased from 122 to 11.5 m^2g^{-1} [15]. This technique can be adapted by adding urea to the sol, which can result in titania with higher specific surface area as well as larger pore size of titania nanoparticles. Urea showed a retarding effect on the transformation of titania from anatase to rutile [22]. In 2009, the composite of zinc oxide and titania were prepared by sol-gel process. The results indicated that the as-synthesized powder was consisted of anatase TiO_2, zincite ZnO, and $Zn(OH)_2$ phase. Upon the heating up to 220 °C all of $Zn(OH)_2$ phase was transformed into ZnO. Increasing calcination temperature up to 680 °C produced Zn_2TiO_4 and $ZnTiO_3$ solid solution in ZnO/TiO_2 system. With an increase in temperature, the amount of $ZnTiO_3$ phase decreased in way that it totally disappeared at 900 °C and transformed into Zn_2TiO_4. The specific surface area of the samples after being calcined at 220, 420, and 800 °C were 51.24, 46.32, and 26.28 m^2g^{-1}, respectively [19]. Increase in particle size and aggregation occurred after high temperature treatment. Tian et al. prepared N-doped titania/zinc oxide composite powder by sol-gel method whereas ammonia was used as a nitrogen source. The phase transformation of anatase to rutile was retarded via the ammonia treating process, leading to the presence of anatase phase in the composite. Crystallite size of the composite powder was about 15 nm [5]. The biggest advantage of N-doping, compared to undoped titania, is their lowered excitation energy [23]. N-doping is reported to be a good way for the preparation of TiO_2 photocatalysts with enhanced photocatalytic activity and modified the particle and crystallite size [24].

Sol-gel process is considered as one of the most promising alternative because it presents a number of advantages such as low sintering temperature, versatility of processing and homogeneity at molecular level [25]. However, the limit of this method is that strong reactivity of alkoxide toward water often results in uncontrolled precipitation. The parameters effect to rate reaction of sol-gel is solution pH, molar ratio of reactants, aging time and temperature. The reaction of sol-gel process follows Equation (1)-(3).

Hydrolysis:

$$\text{M-O-R} + H_2O \longrightarrow \text{M-OH}+\text{R-OH} \qquad (1)$$

Condensation:

$$\text{M-OH} + \text{HO-M} \longrightarrow \text{M-O-M}+H_2O \qquad (2)$$

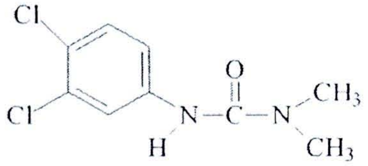
$$\text{M-O-R}+\text{HO-M} \longrightarrow \text{M-O-R}+\text{R-OH} \qquad (3)$$

whereas, M is Metal and OR is Alkoxyl group

2.2 Diuron

Diuron [3-(3,4-dichlorophenyl)-1,1-dimethylurea], is a long acting herbicide,belonging to the family of halogenophenylureas. It has been one of the most commonly used herbicides for more than 40 years. Diuron has been reported to be highly toxic for some non-target organisms. Diuron in agricultural may penetrate through soil slowly and contaminate groundwater. It may pose potential environment and health problems from runoff waters coming from agricultural land where diuron has been used extensively [26].Therefore, diuron was selected for investigation of the photocatalytic degradation in this research. There are some human health concerns about the toxicity of some impurities in the active constituent of diuron as well. Its properties are shown in Table 2.3.

Table 2.3 Physicochemical properties of diuron.

Structure formula	
Molecular weight	233.10 g/mol
Molecular formula	$C_6H_{10}Cl_2N_2O$
Melting point	158 – 159°C
Vapor pressure	0.0041 Pa at 30°C
Appearance	White crystalline solid
Synonyms	Cekiuron; Crisuron; Dailon; Di-on; Krovar; Unidron; Vonduron; Xarmex; etc.
Solubility	42 ppm in water at 25°C
Toxicity	The concentrated material may cause irritation to eyes and mucous membrane, but a 50% -water paste is not irritating to the intact skin of mammal.
Half-life	372 days in soil [27]

2.3 Photocatalytic Degradation

Photocatalytic process is a technology for oxidation/degradation of organic contaminants in environmental control. It can use sunlight, which is available in abundance, as the energy source to initiate the photodecomposition of pollutants. The end products of this treatment process are usually harmless compounds such as carbon dioxide, water and inorganic ions such as chloride and nitrate. It has been widely used as an alternative physical-chemical process for the elimination of toxic and hazardous organic substances in wastewater, drinking water, and air. In this process, a semi-conductor activated by ultra-violet (UV) radiation is used as a catalyst to destroy organic contaminants.

The photocatalysis can be defined as the acceleration of a photoreaction by the presence of a semiconductor catalyst that can be activated by the absorption of light of energy greater than its band gap. Since the contaminants are present in the aqueous phase, while the semiconductor is solid, this process can be called heterogeneous photocatalysis process. The generations of electron-hole pairs are represented in Eq. (4). The photo-generated holes and electrons give rise to oxidation and reduction processes, respectively. In an aqueous solution, water molecules adsorb onto surface of the catalyst. They are oxidized giving rise to $OH^{\bullet}$ radicals. As the process is usually carried out in aerobic conditions, the species to be reduced is oxygen, generating the superoxide radical as following Eq. (5) to (7). Organic pollutants adsorb onto the surface of the catalyst are subsequently oxidized by $OH^{\bullet}$ radicals.

$$\text{Semiconductor} + h\nu \rightarrow h^{+} + e^{-} \qquad (4)$$

$$h^{+} + H_2O_{ads} \rightarrow OH^{\bullet} + H^{+} \qquad (5)$$

$$h^{+} + OH^{-}_{ads} \rightarrow OH^{\bullet} \qquad (6)$$

$$e^{-} + O_2 \rightarrow O_2^{-} \qquad (7)$$

Support of the $OH^{\bullet}$ radical as the main reactive oxidant derives from the observation that intermediates detected during the photocatalytic degradation of halogenated aromatic compounds are typically hydroxyl structures, as those found when similar aromatics react with a known source of $OH^{\bullet}$ radicals. The hydroxyl radical has a very short half-life of approximately 10^{-9} seconds and a high reactivity [28].

The mechanism of the photocatalytic degradation of aqueous organic compound on anatase titania can be expressed by a series of advanced oxidation process as following [28].

1) Absorption of efficient photons ($h\nu \geq E_G = 3.2$ eV) by titania

$$(TiO_2) + h\nu \rightarrow e^{-}_{CB} + h^{+}_{VB} \qquad (8)$$

2) Oxygen ionosorption (first step of oxygen reduction)

$$(O_2)_{ads} + e^{-}_{CB} \rightarrow O_2^{\bullet -} \qquad (9)$$

3) Neutralization of OH^{-} groups by photoexcited holes

$$(H_2O \Leftrightarrow H^+ + OH^-)_{ads} + h^+_{VB} \rightarrow H^+ + OH^\bullet \qquad (10)$$

4) Neutralization of $O_2^{\bullet -}$ by protons

$$O_2^{\bullet -} + H^+ \rightarrow HO_2^\bullet \qquad (11)$$

5) Transient hydrogen peroxide formation

$$2\,HO_2^\bullet \rightarrow H_2O_2 + O_2 \qquad (12)$$

6) Decomposition of H_2O_2 and second reduction of oxygen

$$H_2O_2 + e^- \rightarrow OH^\bullet + OH^- \qquad (13)$$

7) Oxidation of the organic reactant via successive attack by $OH^\bullet$ radical

$$R + OH^\bullet \rightarrow R'^\bullet + H_2O \qquad (14)$$

8) Direct oxidation by reaction with holes

$$R + h^+ \rightarrow R^{+\bullet} \rightarrow \text{degradation products} \qquad (15)$$

The mechanisms of photocatalytic degradation of matter on nanosized ZnO powder can be expressed by applying the research of N. Daneshvar [29]. The photocatalytic degradation of organic matter in the solution is initiated by photoexcitation of the semiconductor, followed by the formation of electron-hole pairs on the surface of the catalyst (Eq.16).

$$ZnO + h\nu \rightarrow e_{CB}^- + h_{VB}^+ \qquad (16)$$

The high oxidative potential of the hole (h_{VB}^+) in the catalyst permits the direct oxidation of herbicide into the reactive intermediates (Eq.17).

$$h_{VB}^+ + \text{herbicide} \rightarrow \text{oxidative products of the herbicide} \qquad (17)$$

Very reactive hydroxyl radicals can also be formed either by the decomposition of water (Eq.18) or by the reaction of the hole with OH^- (Eq.19).

$$h_{VB}^+ + H_2O \rightarrow H^+ + OH^\bullet \qquad (18)$$

$$h_{VB}^+ + OH^- \rightarrow OH^\bullet \qquad (19)$$

The hydroxyl radical is an extremely strong, non-selective oxidant that brings about the degradation of organic chemicals as well [30, 31].

Electron in the conduction band ($e_{CB}-$) on the catalyst surface can reduce molecular oxygen to superoxide anion (Eq.20). This radical, in the presence of organic scavengers, may form organic peroxides (Eq.21) or hydrogen peroxide (Eq.22). Electrons in the conduction band are also responsible for the production of hydroxyl radicals, which have been indicated as the primary cause of organic matter mineralization (Eq.23) [10, 30]

$$e_{CB}^{-} + O_2 \rightarrow O_2^{\bullet -} \tag{20}$$

$$O_2^{\bullet -} + \text{herbicide} \rightarrow \text{herbicide} - OO^{\bullet} \tag{21}$$

$$O_2^{\bullet -} + HO_2^{\bullet} + H^{+} \rightarrow H_2O_2 + O_2 \tag{22}$$

$$OH^{\bullet} + \text{herbicide} \rightarrow \text{degradation of the herbicide} \tag{23}$$

Photodegradation is heterogeneous reaction. The reaction is surface reaction since the reaction occurs when the organic matter adsorbs onto the catalyst surface. The reaction is heterogeneous catalytic reaction with the step of reaction as followed: diffusion of reactants, adsorption, surface diffusion, reaction, desorption, and diffusion of products.

2.4 Photocatalytic Degradation of Diuron

Advanced Oxidation Process (AOPs) are alternative and very useful for the degradation of non-biodegradable organic pollutants. They are much more efficient than conventional techniques such as precipitation, flocculation, and adsorption. The chemical processing by AOPs could lead to the complete mineralization of pollutants. AOPs are based on the generation of the hydroxyl radicals and use them as primary oxidant for the degradation of organic pollutants.

2.4.1 The kinetic of photodegradation of diuron

Several papers on photocatalytic processes have been presented in the recent years [1, 6, 10, 18, 26, 29, 32-36]. The degradation rate of diuron depending on parameters influencing the oxidation such as pH value, light intensity, and concentration of photocatalyst. According to these papers, the photocatalytic processes are able to degrade non-biodegradable organic pollutants. They have also found that the kinetic model suitable for, the photocatalytic reaction is the Langmuir – Hinshelwood model, in which the substrates must adsorb on the catalyst surface sites for bond breaking or bond formation. The adsorption of substrates and the availability of sites are important parameters in photocatalytic reactions. The rate of substrate conversion is proportional to the available active sites. As the reaction proceeds, the amount of substrate adsorbed on the catalysts surface will decrease until the substrate is completely converted. In general, kinetic models are often formulated to describe photocatalytic reactions with respect to the initial substrate concentrations. For the Langmuir – Hinshelwood kinetic model, it is assumed that the reaction occurs on the surface and the reaction rate (r) is proportional to the fraction of surface coverage by the substrate (θ):

$$r = -\frac{dC}{dt} = k_r\theta = k_r\frac{KC}{1 + KC} \tag{24}$$

where k_r is the reaction rate constant, K is the adsorption constant and C is the substrate concentration at any time t. When the solution is highly diluted, the term KC can be neglected. Previously several researchers approximated Langmuir-Hinshelwood kinetics to first order by assuming the term $KC << 1$ [37, 38]. Thus the Langmuir-Hinshelwood kinetic expression can be written as equation (25). The constants k_r and K can be calculated from the corresponding integrated expression in equation (26).

$$r = -\frac{dC}{dt} = k_r KC \tag{25}$$

$$ln\frac{C_0}{C} + K(C_0 - C) = k_r Kt \tag{26}$$

The L-H model includes adsorption and reaction data. Moreover, the results of some papers indicated that the photocatalytic process is very efficient because it often achieves a complete mineralization of organics. Bamba et al. have investigated the photodegradation of diuron from aqueous solution by UV irradiation in the presence of commercial TiO_2 (P25 and PC500). The results of kinetic study showed that kinetic model for diuron photocatalytic degradation follows the Langmuir – Hinshelwood model. At concentration of diuron 10 ppm the pseudo – first order Langmuir – Hinshelwood rate coefficient were 1.787 and 0.576 ppm/min and the constant of adsorption equilibrium of Langmuir – Hinshelwood were 0.801 and 0.451 ppm^{-1} for the use of TiO_2 – P25 and TiO_2 PC500 respectively [35]. The kinetic rate constant of photodegradation of diuron depend on initial diuron concentration, catalyst loading, pH, and temperature [35, 39, 40]. High catalyst loading produces great number of

OH radicals and accelerates the reaction. In addition, it is media to the adsorbed diuron. Amount of catalyst loading and particle size of catalyst affect on photodegradation rate such that the degradation is increased when the catalyst loading is increased.

2.4.2 Diuron degradation products

The disappearance of the initial compound is not sufficient to demonstrate the effectiveness of the photocatalytic process because the intermediate compounds formed during the reaction could be even more toxic and resilient towards degradation than the parent compound. It is hence of interest not only to monitor the degradation of the parent compound but also to identify the intermediate compounds formed. In general, the oxidation of straight-chained hydrocarbon is relatively easy, while dearomatisation of aromatic compounds has been found to be harder, taking longer time and involves the formation of many intermediate compounds before mineralization is achieved.

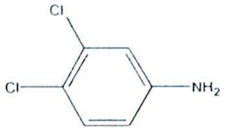
The degree of degradation of diuron was obviously affected by photocatalyst amount, initial concentration of diuron, pH of solution, and temperature [18, 35]. For the photocatalytic degradation of the diuron contaminants, which has been investigated in the past, Klongdee et al. studied the degradation of diuron in aqueous solution by photocatalyzed oxidation, using synthesized titania as catalyst. Titania was synthesized by the thermal decomposition method. The results indicated that the conversions achieved from the prepared titania were about 70-80% within 6 hours, using standard UV lamps, while about 99% conversion was achieved under solar irradiation. The enhanced photocatalytic activity was the result from higher crystallinity of the synthesized titania. The presence of oxygen as an electron scavenger in the system was required for the reaction to progress [6]. However, the degradation rate of diuron depending on parameters influencing the oxidation such as pH value, light intensity, and concentration of photocatalyst [2]. The mineralization reaction (first order reaction) can be estimated as follows [1] :

$$C_9H_{10}Cl_2N_2O + 13O_2 \longrightarrow 2HCl + 2HNO_3 + 9CO_2 + 3H_2O$$

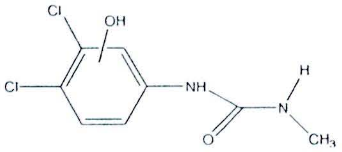
The organic intermediates formed during the degradation of diuron could be classified into two categories. One is the non-chlorinated intermediates, another is the chlorinated and nitrated intermediates [2]. Most detected degradation products are constituted by diuron de-methyl derivatives, such as DCPMU [3-(3,4-dichlorophenyl)-1-methylurea], DCPU [3-(3,4-dichlorophenylurea)], and 3,4-DCA (3,4-dichloroaniline) [41] The structures of the photoproducts are represented as follows: [1]

Compound 1

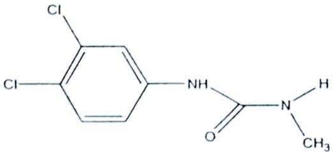
Compound 2



Compound 3



Compound 4



The product compound number 1, 2, and 4 were identified as the compounds resulting from the elimination of alkyl groups from diuron. The product compound number 3 was found to be the product in which hydroxyl group was added to benzene ring of diuron. Therefore the possible degradation pathway for diuron based on the intermediate products was proposed in Figure 2.3 [1].

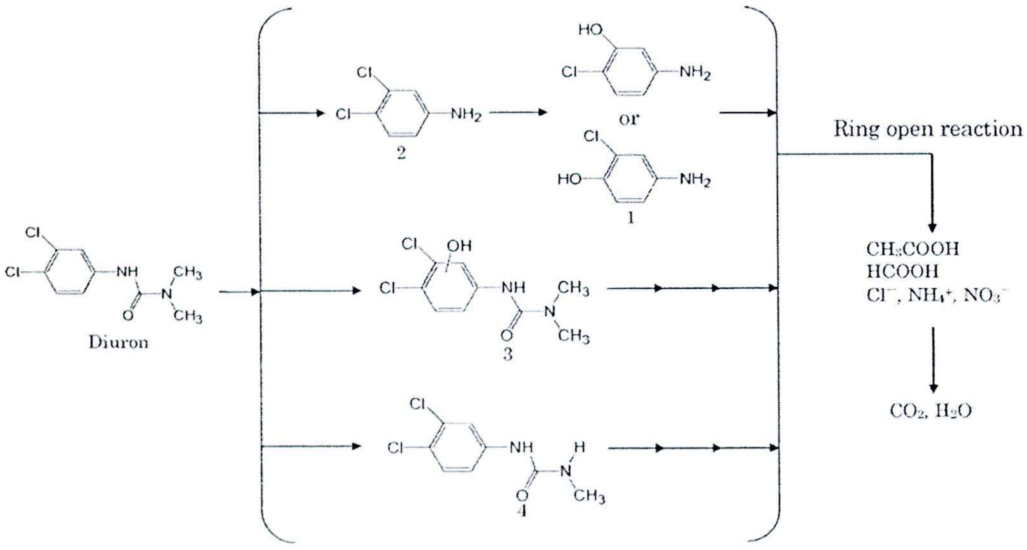
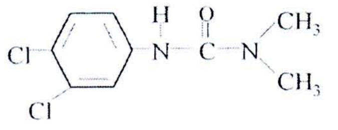


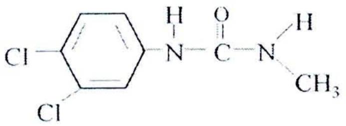
Figure 2.3 Proposed degradation mechanism of diuron by the photocatalytic system [1].

The previous researches have reported that different conditions of degradation produce different intermediate products. For instance, Carrier et al. investigated intermediate products of photocatalytic degradation using titania as photocatalyst. The possible degradation pathway for diuron was proposed in Figure 2.4. The reported steps of degradation included dehalogenation of the aromatic ring, hydroxylation of the aromatic ring and of the side chain, and demethylation [42]. Then they investigated the removal of diuron and thermal degradation products under catalytic wet air oxidation condition, using Ru/TiO_2 as catalyst at 140 °C and 180 °C. During the thermal degradation of diuron, three main intermediate compounds were formed, namely 3,4-dichloroaniline (DCA), dimethylamine (DMA), and 3-(3,4-dichlorophenyl)-1,1-methylurea. Degradation pathways of diuron by the catalytic wet air oxidation based on the identified intermediate products of the reaction, was proposed in Figure 2.5. The first step was a thermal degradation of diuron into DCA and DMA. The next step was a series of oxidation process of DCA that rapidly eliminated chlorine, opened the aromatic ring to yield small organics acids and leaded to inorganic species. Nitrogen in DCA was mainly transformed into NH_4^+. The carboxylic acids formed (oxalic acid and acetic acid) reacted with DCA to form traces of 3,4-dichlorophenylamide and 3,4-dichlorophenylacetamide. DMA was more resistant and high temperature of the reaction was necessary. At 180 °C, DMA was converted into methylamine (MA), ammonium ions and nitrates. The higher temperature favoured the formation of nitrates [43]. Oturan et al. identified five kinds of intermediate products from electrochemical advanced oxidation method called "electro-Fenton process". Several aromatic by-products, mainly formed by oxidation of the N-terminal group, accompanied by hydroxylation of the aromatic cycle and/or side methyl group, and aromatic dehalogenation were identified. Further steps involved the oxidative opening of the aromatic ring, leading to carboxylic acids and inorganic ions. Identification of the diuron degradation products was conducted by LC-MS and the results are represented as follow: [44]

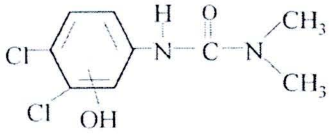
3-(3,4-Dichlorophenyl)-1,1-dimethyl urea (diuron)

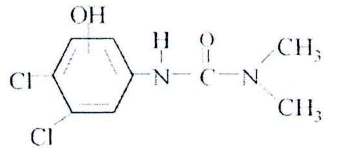
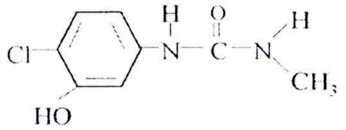
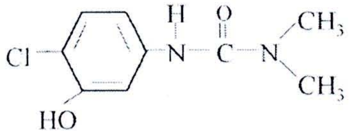


3-(3,4-Dichlorophenyl)-1,1-methyl urea



3-(3,4-Dichloro-hydroxyphenyl)-1,1-dimethyl urea



3-(Trihydroxyphenyl)-1,1-dimethyl urea	
3-(3-Hydroxy-4-chlorophenyl)-1,1-methyl urea	
3-(3-Hydroxy-4-chlorophenyl)-1,1-dimethyl urea	

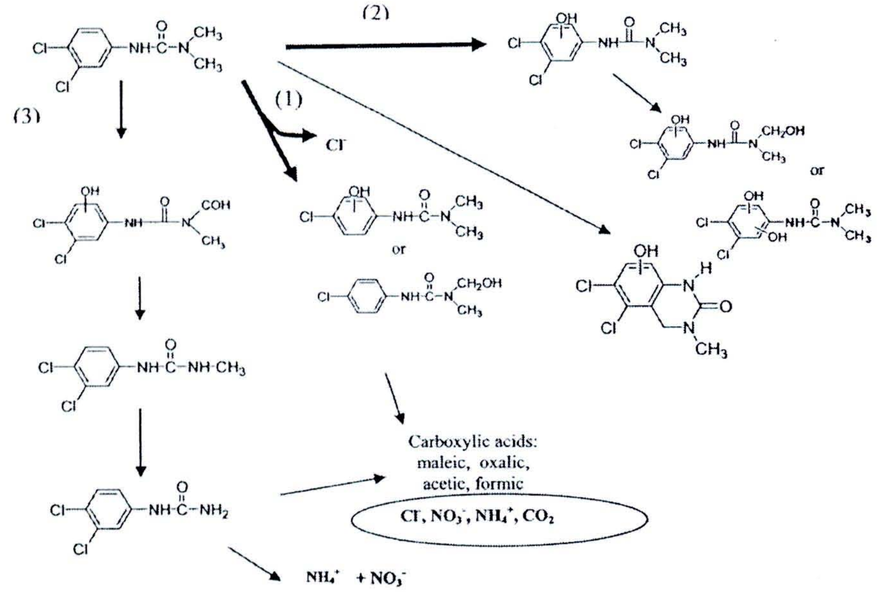


Figure 2.4 Degradation pathways of diuron by the TiO_2 as photocatalyst [42].

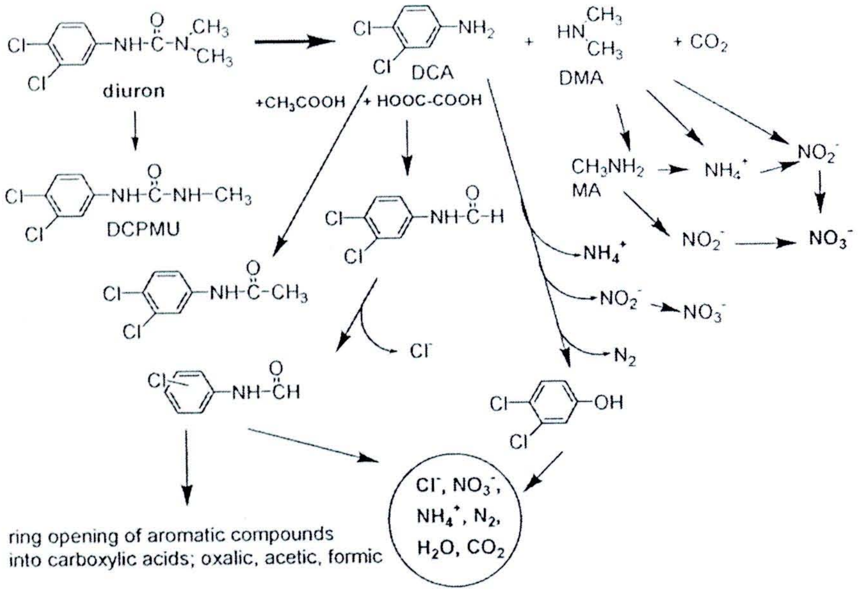


Figure 2.5 Degradation pathways of diuron by catalytic wet air oxidation [43].