PHOTOCATALYTIC REMOVAL OF 2,4-DICHLOROPHENOXYACETIC ACID AND QUINCLORAC HERBICIDES BY AN IMMOBILIZED SYSTEM OF CARBON COATED, NITROGEN DOPED AND POLYENE SENSITIZED TiO$_2$

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by

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In the Name of Allah, the Most Gracious and Merciful

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LIST OF ABBREVIATIONS AND SYMBOLS

2,4-D	2,4-dichlorophenoxyacetic acid
a.u.	Arbitrary units
AOPs	Advanced oxidation processes
$CNTiO_2$	Carbon coated nitrogen doped TiO_2
$CNTiO_2$/EP	Immobilized carbon coated nitrogen doped TiO_2
$CNTiO_2$/EP-10h	Photo-etched immobilized carbon coated, nitrogen doped and polyene sensitized TiO_2
e^-	Electron
EDX	Energy dispersive X-ray
E_g	Band gap energy
ENR_{50}	Epoxidized natural rubber
FESEM	Field emission scanning electron microscopy
FL	Fluorescence
FTIR	Fourier-transform Infra red
h^+	Positive hole
Hv	Photonic energy
HPLC	High performance liquid chromatography
IC	Ion chromatography
LC-MS	Liquid chromatography-Mass spectrometry
m/z	Mass to charge
Nm	Nanometer
•OH	Hydroxyl radical
PVC	Polyvinyl chloride

QNC	Quinclorac
RR4	Reactive red 4
TOC	Total organic carbon
TiO_2	Titanium dioxide
TiO_2/EP-10h	Photo-etched immobilized titanium dioxide
UV	Ultraviolet
UV-Vis DRS	UV-Vis diffuse reflectance spectroscopy
Vis	Visible light
XPS	X-ray photoelectron spectroscopy

PENYINGKIRAN PEMFOTOPEMANGKINAN RACUN HERBISID ASID 2,4-DIKLOROFENOKSIASETIK DAN KUINKLORAK OLEH SISTEM PEGUN TiO$_2$ TERSALUT KARBON, TERDOP NITROGEN DAN TERPEKA POLIENA

ABSTRAK

Suatu sistem pegun TiO$_2$ bersalut karbon, terdop nitrogen dan terpeka poliena (CNTiO$_2$/EP-10h) telah dibangunkan menggunakan getah asli terepoksida (ENR$_{50}$) dan polivinil klorida (PVC) sebagai pengikat melalui kaedah penyalutan celup. Jumlah optimum fotomangkin dan pengikat PVC dalam formulasi penyalutan masing-masing adalah 6 g dan 0.8 g, manakala 2.29 mg cm^{-2} adalah jumlah terbaik pemuatan komposit fotomangkin. Proses fotopunaran untuk 10 jam (10h) telah mengurangkan tenaga jurang jalur fotomangkin daripada 2.91 kepada 2.86 eV, menghasilkan permukaan fotomangkin yang amat berliang serta mengoksidakan pengikat PVC menjadi poliena berkonjugat yang memekakan TiO$_2$. Kecekapan CNTiO$_2$/EP-10h bagi degradasi pemfotopemangkinan asid 2,4-diklorofenoksiasetik (2,4-D) telah ditentukan di bawah penyinaran cahaya UV-Vis, nampak dan suria. Penyingkiran pemfotopemangkinan 2,4-D terbaik telah diperolehi di bawah cahaya UV-Vis diikuti oleh suria dan cahaya nampak. Keadaan teroptimum bagi penyingkiran pemfotopemangkinan 2,4-D oleh CNTiO$_2$/EP-10h di bawah penyinaran cahaya UV-Vis, nampak dan suria telah ditemui pada pH 3 dengan kadar aliran pengudaraan pada 40 mL min^{-1}. Pemineralan lengkap 2,4-D oleh CNTiO$_2$/EP-10h telah dicapai selepas 6 jam di bawah penyinaran cahaya suria. Analisis LC-MS mengesan diklorofenol, diklorokatekol, diklororesorsinol, klorohidrokuinon, hidroksihidrokuinon, fenol, asid mukonik dan fumarik sebagai produk perantaraan

daripada penyingkiran pemfotopemangkinan 2,4-D. Penggunaan CNTiO$_2$/EP-10h telah dilanjutkan kepada degradasi pemfotopemangkinan kuinklorak (QNC) Penyingkiran QNC oleh CNTiO$_2$/EP-10h menjadi lebih cepat dalam urutan penyinaran cahaya nampak < UV-Vis < suria. Degradasi pemfotopemangkinan QNC teroptimum telah diperolehi pada pH 3 dengan penambahan 30 μL H$_2$O$_2$. Penambahan H$_2$O$_2$ semasa proses pemfotopemangkinan dan penjanaan semula mengakibatkan aktiviti pemfotopemangkinan mampan CNTiO$_2$/EP-10h bagi penggunaan terkitar semula. Pemineralan hampir lengkap QNC telah dicapai selepas 12 jam di bawah penyinaran cahaya suria. 3,7-Diklorokuinolina-8-ol dan 3,7-diklorohidroksikuinolina-8-asid karboksilat telah dikesan daripada analisis LC-MS sebagai produk perantaraan daripada degradasi pemfotopemangkinan QNC oleh CNTiO$_2$/EP-10h. CNTiO$_2$/EP-10h yang direka menunjukkan kebolehgunaan semula yang cemerlang dengan aktiviti pemfotopemangkinan yang mampan sehingga sepuluh applikasi kitaran semula dalam penyingkiran 2,4-D dan QNC.

PHOTOCATALYTIC REMOVAL OF 2,4-DICHLOROPHENOXYACETIC ACID AND QUINCLORAC HERBICIDES BY AN IMMOBILIZED SYSTEM OF CARBON COATED, NITROGEN DOPED AND POLYENE SENSITIZED TiO$_2$

ABSTRACT

An immobilized system of carbon coated, nitrogen doped and polyene sensitized TiO$_2$ (CNTiO$_2$/EP-10h) was fabricated using epoxidized natural rubber (ENR$_{50}$) and polyvinyl chloride (PVC) as the binders through a dip coating technique. The optimum amount of photocatalyst and PVC binder in the coating formulation were 6 g and 0.8 g, respectively, while 2.29 mg cm^{-2} was the best amount of photocatalyst composite loading. The photo-etching process for 10 hours (10h) reduced the band gap energy of the photocatalyst from 2.91 to 2.86 eV, creating a highly porous photocatalyst surface as well as oxidizing the PVC binder to be a conjugated polyene that sensitized TiO$_2$. The efficiency of CNTiO$_2$/EP-10h for photocatalytic degradation of 2,4-dichlorophenoxyacetic acid (2,4-D) was determined under UV-Vis, total visible and solar light irradiations. The best photocatalytic removal of 2,4-D was obtained under UV-Vis light followed by solar and total visible lights. The optimized conditions for photocatalytic removal of 2,4-D by CNTiO$_2$/EP-10h under UV-Vis, total visible and solar light irradiations were found to be at pH 3 with an aeration flow rate of 40 mL min^{-1}. The complete mineralization of 2,4-D by CNTiO$_2$/EP-10h was achieved after 6 hours under solar light irradiation. The LC-MS analysis detected dichlorophenol, dichlorocatechol, dichlororesorcinol, chlorohydroquinone, hydroxyhydroquinone, phenol, muconic and fumaric acid as the intermediate products from the photocatalytic removal of 2,4-D.

The application of CNTiO$_2$/EP-10h was also extended to the photocatalytic degradation of quinclorac (QNC). The removal of QNC by CNTiO$_2$/EP-10h became faster in the order of total visible < UV-Vis < solar light irradiation. The optimized photocatalytic degradation of QNC was obtained at pH 3 with an addition of 30 μL of H$_2$O$_2$. The addition of H$_2$O$_2$ during photocatalytic degradation and regeneration processes resulted in the sustainable photocatalytic activity of CNTiO$_2$/EP-10h for the recycled application. Almost complete mineralization of QNC was achieved after 12 hours under solar light irradiation. 3,7-Dichloroquinoline-8-ol and 3,7-dichlorohydroxyquinoline-8-carboxylic acid were detected from LC-MS analysis as the intermediate products from the photocatalytic degradation of QNC by CNTiO$_2$/EP-10h. The fabricated CNTiO$_2$/EP-10h exhibited excellent reusability with a sustainable photocatalytic activity up to ten recycled applications in the removal of 2,4-D and QNC.

CHAPTER ONE

INTRODUCTION AND LITERATURE REVIEWS

1.1   Environmental problem

The supply of clean water and degradation of water quality becomes a worldwide concern nowadays due to the high water demand. The growths in populations, urbanization, economic and industrial sectors are the major factors contributing to high demand of fresh water (Bennett, 2000). However, in line with this rapid growth, water sources are becoming more polluted and formidable to treat. Rivers are being polluted by organic compounds, toxic pesticides, and manure emissions originating from the respective industries, which later lead to worldwide contamination (Lee and Park, 2013). In fact, the United Nations estimated that by 2025, two-thirds of the global population may suffer serious water shortage problems if no corrective measures are taken (Trinh et al., 2013). One of the corrective measurements is through wastewater treatment.

Wastewater is defined as the discharged water from any municipal or industrial source. Most wastewater originates from cities, as well as industrial and agricultural sectors. The untreated wastewater usually consists of suspended solids, colorant and also chemicals such as toxic organic compounds, cyanide, phenol, phosphorus and heavy metals (Rashidi et al., 2015). These pollutants need to be removed from the wastewater before discharging into water sources in order to reduce its negative impacts towards the environment.

1.2 Wastewater treatments

Generally, the typical wastewater treatment consists of three step-wise processes, which are primary, secondary and tertiary stages. In the primary stage, the collected wastewater undergoes basic screening and filtration processes to separate the suspended solid waste from the water and to reduce its biochemical oxygen demand (BOD) value. BOD value is important in wastewater treatment as it is an indicator to observe the water quality by evaluating the amount of oxygen consumed by the microorganism to break down the organic compounds present in wastewater. In the second stage, the wastewater is treated using biological processes to degrade the remaining dissolved organic matters. Primary and secondary stages of wastewater treatment can reduce 30 % and 90 % of the BOD value, respectively (Malik et al., 2015).

The tertiary step is introduced into the wastewater treatment in order to remove persistence pollutants such as phenols, pesticides, and dyes which cannot be fully treated using the filtration and biological processes. The commonly applied processes in the tertiary treatment system include ultrafiltration (Goren et al., 2008; Leyva-Díaz et al., 2015), coagulation-flocculation (Lee and Park, 2013) and reverse osmosis (Farias et al., 2014; Herzberg et al., 2010). Table 1.1 shows the advantages and disadvantages of several common techniques used for wastewater treatment. However, after undergoing three stages of treatment, most of the treated water does not yet achieve the acceptable quality level for discharge; i.e., COD of 200 mg L^{-1} (Environment Quality Act, 1974). Therefore, further treatment stage is required to achieve the desired water quality of the discharged wastewater. This stage may include the application of the advanced oxidation process (AOP), which is effective

for removal of chemically and biologically stable contaminants (Leyva-Díaz et al., 2015).

Table 1.1: The advantages and disadvantages of common wastewater treatment techniques.

Process	Advantages	Disadvantages
Biological treatment (Lee and Park, 2013)	• highly reliable • economical and safe • high load operation can be processed	• efficiency of processing not stable • high level of sludge
Reverse osmosis (Farias et al., 2014; Herzberg et al., 2010)	• effective in reducing eco-toxicity and genotoxicity of secondary treated wastewater • efficient in removing inorganic contaminants	• reduced performance due to biofouling • large economic burden due to chemical cleaning and short membrane life
Ultrafiltration (Goren et al., 2008)	• good effluent quality • suitable for unrestricted irrigation • improvement in disinfection of product	• low retention of organic content • irreversible fouling
Coagulation (Lee and Park, 2013)	• high efficiency for suspended solid removal	• excessive sludge • use chemicals to coagulate the pollutants

1.3   Advanced Oxidation Processes (AOPs)

The advanced oxidation processes (AOPs) are widely used to degrade persistent pollutants such as pesticides, dyes, and phenols from wastewater. AOPs have been accepted as highly efficient processes for removing persistence pollutants and has been used together with the biological process to enhance the pollutant

degradation efficiency (Leyva-Díaz et al., 2015). AOPs generate hydroxyl radicals (•OH), a highly oxidizing species (E^0=2.80 V) which takes part in degrading the organic pollutants in wastewater. The use of AOPs for removal of pollutants has several advantages including:

1) Fast reaction rates and simultaneous degradation of multiple pollutants due to highly oxidizing and non-selective nature of hydroxyl radicals (Antonopoulou et al., 2014).

2) Complete mineralization of the pollutant with water, carbon dioxide and inorganic ions as final byproducts (Ribeiro et al., 2015).

3) The production of •OH and other radical species via various methods depending on the specific requirements for the degradation of different pollutants (Antonopoulou et al., 2014).

One drawback of AOPs for wastewater treatment is the presence of scavenger species in most wastewater. The scavenger species present in real wastewater includes organic compounds such as proteins, carbohydrates and humic acid as well as inorganic ions such as carbonates, bicarbonates, nitrates and dissolved sulfides. These scavenger species react with hydroxyl radicals, thus leaving less hydroxyl radicals to degrade the pollutants (Ribeiro et al., 2015).

AOPs can be carried out either as homogeneous or heterogeneous modes depending on the phase of the reaction. Homogeneous AOPs take place in a single phase while the heterogeneous AOPs occur when the reaction between the substrate and the catalyst is in two different phases. The examples of homogenous AOPs are (i) ozone (O_3) based process, (ii) wet peroxide oxidation utilizing hydrogen peroxide (H_2O_2) as the oxidizing agent and (iii) Fenton-based process. The chemical process

in homogeneous AOPs depends solely on the reaction between added oxidant and the pollutant. On the other hand, heterogeneous AOPs depend not only on the interaction between oxidant and pollutant, but also on the adsorption of pollutant and desorption of byproduct at the active site of the catalyst. Some examples of commonly used heterogeneous AOPs are (i) heterogeneous photocatalyst in the presence of light irradiation, (ii) catalytic wet peroxide oxidation where heterogeneous catalyst is used, (iii) catalytic ozonation and (iv) heterogeneous Fenton-like processes (Ribeiro et al., 2015).

1.4   Heterogeneous photocatalysts

The heterogeneous photocatalysts are extensively used in AOPs for the removal of contaminants from wastewater. One of the common heterogeneous photocatalysts is semiconductor-based photocatalyst. The semiconductor-based photocatalyst can be described as a metal semiconductor which can produce electron (e^-) and holes (h^+) when it is exposed to the photon of energy (*hv*) that is equal or higher than its band-gap energy (E_g). In order to be an ideal photocatalyst, a semiconductor must be chemical- and photo-stable, able to adsorb pollutant under efficient photonic activation, cheap and easily available (Ribeiro et al., 2015). Besides, the photocatalyst needs to have the ability to be used at room temperature and pressure, giving complete mineralization without secondary pollutants and can be used for recycled applications (Lee and Park, 2013). Table 1.2 shows the examples of semiconductors which can be used as photocatalyst together with its band gap energy.

Table 1.2: Semiconductor photocatalysts with their band gap energy (Robert, 2007).

Semiconductor photocatalyst	Band gap energy (eV)
TiO_2	3.2
SnO_2	3.9
ZnO	3.2
WO_3	2.8
CdS	2.5
CdSe	2.5
GaAs	1.7
GaP	1.4

Unlike the conventional methods for wastewater treatment, heterogeneous photocatalyst works by breaking down the complex molecule of pollutants into smaller and less hazardous substances. This method produces no residue and there is no need for secondary treatment. Among heterogeneous photocatalyst, titanium dioxide (TiO_2) is the most commonly used photocatalyst in AOPs. This is due to the degradation of pollutants via the oxidation process by the photo-generated holes and hydroxyl radicals generated by TiO_2. Besides, the recombination process of holes and electrons in TiO_2 can be prevented by the addition of electron acceptors such as O_2 and H_2O_2 which produces more reactive oxygen species for degradation of pollutants, thus enhancing its photocatalytic efficiency. In addition, TiO_2 can also be operated using solar light irradiation which reduces the operating cost. Thus, the interest in TiO_2 as a photocatalyst has gained in these recent years (Karci, 2014).

1.5   Titanium dioxide (TiO$_2$) as a photocatalyst

Titanium dioxide (TiO$_2$) is known as an excellent photocatalyst for environmental purification. Till now, TiO$_2$ is the most used photocatalysts based on its benefit-cost ratio, as well as its suitable optical and electronic properties and good chemical stability (Ullah et al., 2015). TiO$_2$ is present in two metastable phases (anatase and brookite) and one stable phase (rutile). Each phase has different crystalline behaviors which are tetragonal for rutile and anatase while brookite is orthorhombic in nature. These three crystallines comprise of TiO$_6$ octahedra connected differently by corners and edges. Rutile phase has two shared octahedral edges to form linear chains along the [0 0 1] direction and TiO$_6$ chains are linked to each other through corner-shared bonding. For anatase, each octahedron shares four edges with other four octahedra to form a zig-zag structure. In the brookite structure, each octahedron shares three edges and the octahedral arrangement produce a crystalline structure with tunnels along the c-axis (Di Paola et al., 2008). Figure 1.1 shows the crystalline structures of TiO$_2$ in the three different phases.
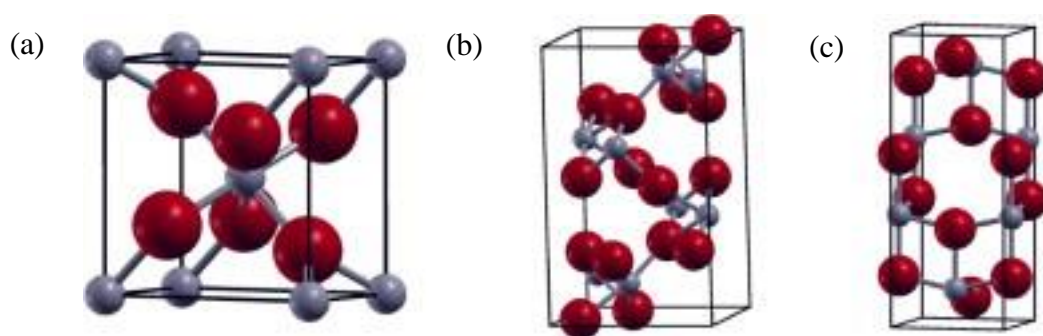
Figure 1.1: Crystalline structures of (a) rutile (b) brookite and (c) anatase TiO$_2$ (Esch et al., 2014).

Anatase phase has generally been accepted as the most photocatalytic active phase for TiO_2 (Di Paola et al., 2008; Zangeneh et al., 2015). On the other hand, rutile phase TiO_2 does not have good photocatalytic properties as compared to anatase TiO_2. The lower photocatalytic activity of rutile TiO_2 is due to the following reasons (Zangeneh et al., 2015):

(i)   Larger particle size due to higher temperature applied during preparation of rutile TiO_2.

(ii)   Higher electron-hole recombination rate, resulting in the limited amount of hydroxyl radicals on TiO_2 surface.

(iii)   Lower photocatalytic efficiency as a result of lower electron lying at the conduction band edge.

The combination of anatase and rutile phase of TiO_2 shows excellent photocatalytic activity. This is due to the band alignment between rutile and anatase TiO_2 that lowering the effective band gap of composite and gives better electron-hole separation (Scanlon et al., 2013). Degussa P-25 is the commonly used, highly photoactive form of TiO_2 that is comprised of 20-30 % rutile and 70-80 % anatase phase of TiO_2. Degussa P-25 has an average particle size of 21 nm and is commonly used as standard reference photocatalyst for comparison of photo-activity with other newly synthesized photocatalysts (Nawi and Zain, 2012).

TiO_2 can act as photocatalyst when it is photo-activated by ultraviolet (UV) irradiation. The irradiation light energy must exceed TiO_2 semiconductor band gap energy (3.0 and 3.2 E_g for rutile and anatase, respectively) to excite the electron (e^-) from TiO_2 valence band (vb) to TiO_2 conduction band (cb) (Oliveira et al., 2011). This excitation process leaves holes (h^+) at the valence band of TiO_2. Later, the

electron (e^-) and holes (h^+) can either be recombined, or react with oxidizing species (H_2O, OH^-, organic compounds) and reducing species (O_2) to produce reactive species such as hydroxyl radicals ($\bullet OH$), superoxide anions ($O_2\bullet^-$) and hydroperoxyl radicals ($\bullet OOH$) on the TiO_2 surface. These reactive radical species are important for the degradation process of organic pollutants. The mechanisms of TiO_2 photo-activation and photocatalytic reaction are shown in Equations 1.1 to 1.9 (Zangeneh et al., 2015):

$$TiO_2 + h\nu \rightarrow TiO_2\ (e_{cb}^- + h_{vb}^+) \tag{1.1}$$

$$TiO_2\ (h_{vb}^+) + H_2O \rightarrow TiO_2 + H^+ + \bullet OH \tag{1.2}$$

$$TiO_2\ (h_{vb}^+) + OH^- \rightarrow TiO_2 + \bullet OH \tag{1.3}$$

$$TiO_2\ (e_{cb}^-) + O_2 \rightarrow TiO_2 + O_2\bullet^- \tag{1.4}$$

$$O_2\bullet^- + H^+ \rightarrow HO_2\bullet \tag{1.5}$$

$$HO_2\bullet + HO_2\bullet \rightarrow H_2O_2 + O_2 \tag{1.6}$$

$$TiO_2\ (e_{cb}^-) + H_2O_2 \rightarrow \bullet OH + OH^- \tag{1.7}$$

$$H_2O_2 + O_2\bullet^- \rightarrow \bullet OH + OH^- + O_2 \tag{1.8}$$

$$\text{Organic pollutant} + \bullet OH \rightarrow \text{degradation products} \tag{1.9}$$

Among other photocatalysts, TiO_2 exhibits several advantages such as photo-chemically stable, non-toxic and low cost, which make TiO_2 widely used as the most preferred photocatalyst (Bensaadi et al., 2014; Chen et al., 2007; Grabowska et al., 2012). Previous studies have shown the application of TiO_2 for photocatalytic degradation of various types of organic pollutants such as dyes (Chen et al., 2007; Oliveira et al., 2011; Wang et al., 2004), pharmaceutical compounds (Bensaadi et al.,

2014), herbicides (Krýsová et al., 2003; Trillas et al., 1995), phenol (Grabowska et al., 2012; Marcì et al., 1995) and benzene (Xie et al., 2011).

1.6   Modification of TiO$_2$

TiO$_2$ has been widely acknowledged as the most efficient photocatalyst for the photocatalytic degradation of organic pollutants (Rodríguez et al., 2013; Seck et al., 2012; Zangeneh et al., 2015). However, one major problem of pure TiO$_2$ as a photocatalyst is the need of ultraviolet (UV) light for TiO$_2$ photo-activation which is due to the large band gap energy of TiO$_2$ (E$_g$ = 3.2 eV). This makes TiO$_2$ not suitable for indoor application where the main irradiation is from fluorescent light while sunlight irradiation consists only 3-5 % of UV light while the rest is visible light (Nawawi and Nawi, 2014). To overcome this problem, some modifications of TiO$_2$ have been made to produce a visible light active TiO$_2$. Figure 1.2 shows some modification techniques to synthesize visible light active TiO$_2$.

One of the common techniques to produce visible light active TiO$_2$ is through sensitization of TiO$_2$ photocatalyst with conjugated polymers or dyes. The sensitizer molecule is anchored on the surface of TiO$_2$ via several ways: (a) covalent bonding, (b) ion-pair type association, (c) physisorption, (d) entrapment in cavities or pores and (e) hydrophobic interaction leading to self-assembly of monolayers (Chatterjee and Dasgupta, 2005). Sensitizer molecule assists TiO$_2$ in the photocatalytic degradation process by injecting electrons originating from the initial excitation of sensitizers to the conduction band of TiO$_2$ (Song et al., 2007) thus leads to the production of more hydroxyl radicals by TiO$_2$ for the photocatalytic degradation process of organic pollutants. Several dyes such as acid red 44 (Moon et al., 2003), eosin-Y (Abe et al., 2000), methylene blue and rhodamine B (Chatterjee and Mahata,

2002) and conjugated polymers such as poly(fluorine-co-thiophene) (PFT) (Song et al., 2007) and polyvinyl chloride (PVC) (Wang et al., 2012) have been used to produce the visible light active TiO_2.
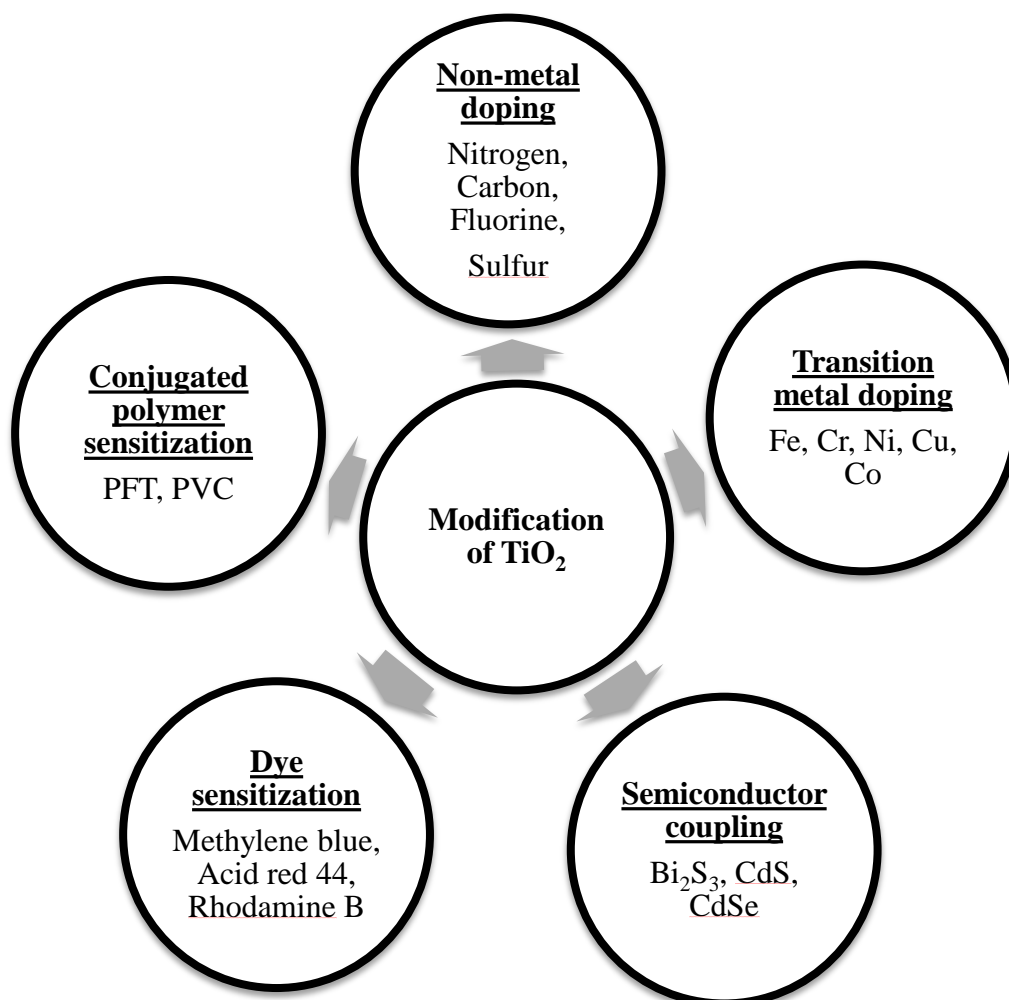
Figure 1.2: Several modification techniques for the production of visible light active TiO_2.

Besides, the visible light active TiO_2 has been produced from the semiconductor coupling of TiO_2 with narrow band gap semiconductors like Bi_2S_3, CdS (Bessekhouad et al., 2004), CdSe (Ho and Yu, 2006), Ag_2S (Li et al, 2016) and $BiFeO_3$ (Hamayun et al., 2016) . The photocatalytic activation mechanism for semiconductor coupling TiO_2 is similar to the sensitization of TiO_2 by dyes and

conjugated polymers. The coupled narrow band gap semiconductor acts as a photosensitizer for TiO_2 as this photocatalyst can be excited by visible light irradiation. The photocatalytic redox reaction under visible light can occur from the photo-excited electron originating from the narrow band gap semiconductor, and the transfer of excited electrons to the TiO_2 particles (Ho and Yu, 2006).

Another commonly used technique to produce visible light active photocatalyst is by doping TiO_2 with transition metals and non-metal elements. In general, the doping process changes the physical properties of TiO_2 such as the lifetime of electron-hole pairs, adsorption characteristic and photochemical stability of TiO_2 (Bessekhouad et al., 2004). For the transition metal doped method, TiO_2 is doped with transition metals such as vanadium, manganese (Yamashita et al., 2002), ferum, cobalt, chromium (Bouras et al., 2007), cerium and lanthanum (Ali et al., 2017), and platinum (Egerton and Mattinson, 2008). The presence of transition metals in TiO_2 matrix shifts the photoactivity of TiO_2 in the visible light region by producing a new energy level in the band gap of TiO_2. Electrons can be excited from the defect state of TiO_2 conduction band by photons with energy equal to *hv*. Besides, the photocatalytic activity of metal-doped TiO_2 is improved as the transition metal traps the electron and prevents the recombination process during irradiation (Grabowska et al., 2012). However, the doping of transition metal into TiO_2 matrix may lead to loss of crystallinity and phase transformation of TiO_2 to rutile phase, which both results in lower photocatalytic efficiency of TiO_2 (Rehman et al., 2009).

The visible light active TiO_2 has also been widely produced via TiO_2 doping with non-metal elements. In recent studies, TiO_2 has been doped with nitrogen (Asahi et al., 2001; Ihara et al., 2003; Irie et al., 2003; Nawawi and Nawi, 2014), carbon (Wu et al., 2013), sulfur (Han et al., 2011), fluorine (Li et al., 2005),

phosphorus and boron (Basha et al., 2017). Nitrogen is regarded as the most promising dopant. Nitrogen can be easily introduced into the TiO_2 structure as nitrogen has a small ionization potential, similar atomic size as oxygen and high stability in TiO_2 lattice (Linnik et al., 2015). Generally, the visible light response of non-metal doped TiO_2 is explained by three different modification mechanisms:

1) Band gap narrowing due to hybridization of N $2p$ and O $2p$ states in nitrogen doped anatase TiO_2, resulting in a smaller band gap energy and the ability for photo-activation of nitrogen doped TiO_2 with visible light (Asahi et al., 2001).

2) Formation of the impurities level resulting from the substitution of oxygen by the nitrogen atom in TiO_2 (Irie et al., 2003).

3) The presence of oxygen vacancies as oxygen-deficient sites formed in the grain boundaries of TiO_2 (Ihara et al., 2003).

1.7   Nitrogen doped TiO_2

Nitrogen doped TiO_2 gained attention since Asahi et al. (2003) successfully synthesized a visible light active nitrogen-doped TiO_2 film by sputtering TiO_2 in a mixture of N_2/Ar gas. Since then, nitrogen doped TiO_2 has been widely synthesized using various techniques, including sol-gel (Li et al., 2015a; Nolan et al., 2012; Powell et al., 2014), ion implantation, plasma treatment (Lee et al., 2014), plasma-enhanced chemical vapor deposition and hydrothermal method (Li et al., 2015b). Among these techniques, sol-gel is a facile and inexpensive method to synthesize nitrogen doped TiO_2 (Li et al., 2015a).

The doping of nitrogen into the TiO_2 crystal lattice can either be interstitial or substitutional incorporation. Interstitial incorporation is favorable for low concentration of nitrogen while substitutional incorporation is favorable at high

concentration of nitrogen. In interstitial nitrogen doped TiO_2, nitrogen does not replace oxygen within the TiO_2 framework, but is incorporated into interstitial sites within the TiO_2 crystal lattice. This leads to the formation of Ti-O-N as O_2^- is combined with nitrogen to form $(NO)^{3-}$, thus promoting the formation of oxygen vacancies in TiO_2. For substitutional incorporation, oxygen in the lattice is directly replaced by nitrogen, where there must be one oxygen vacancy for every two occupied nitrogen sites due to charge balancing. The incorporation of nitrogen in TiO_2 crystal lattice promotes the oxygen vacancies which later act as the photocatalytic centers (Powell et al., 2014).

The presence of nitrogen in TiO_2 crystal lattice affects the light response of TiO_2 towards visible light. Several theories have been proposed as the mechanism of the visible light response of the nitrogen doped TiO_2. Asahi et al. (2003) proposed that the visible light response of nitrogen doped TiO_2 was due to band gap narrowing from mid-gap level. Besides, the visible light response of nitrogen doped TiO_2 may also be due to paramagnetic nitrogen species such as NO, NO_2, and NO_2^{2-} (Sakatani et al., 2003). On the other hand, Ihara et al. (2003) proposed that oxygen vacancies were responsible for the visible light response of nitrogen doped TiO_2 while the doped nitrogen acted as a blocker of re-oxidation. Figure 1.3 shows the mechanism of visible light photo-activation of nitrogen doped TiO_2.
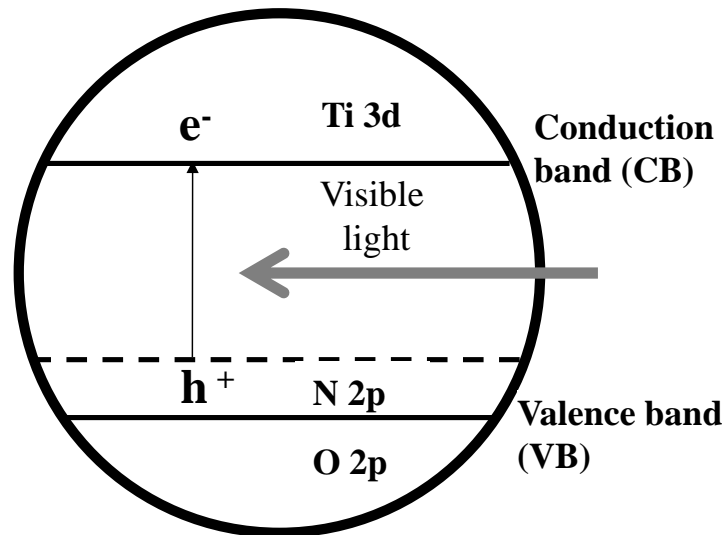
Figure 1.3: Photo-activation of nitrogen-doped TiO_2 by visible light (Khalid et al., 2012).

Recently, the production of nitrogen doped TiO_2 has been extended towards co-doping of TiO_2 with nitrogen and other non-metal and metal dopants. Yu et al. (2015) reported the synthesis of nitrogen and lanthanum co-doped TiO_2 nanosheets through a one-step hydrothermal method. The synthesized nitrogen and lanthanum TiO_2 showed enhanced photocatalytic activity in the visible light region compared to the pure TiO_2 for the photocatalytic degradation of rhodamine B. The presence of nitrogen and lanthanum produces a synergistic effect where nitrogen narrows the band gap of TiO_2 while lanthanum improves the separation efficiency of photoelectrons and holes while also helps in the adsorption of organic pollutants (Yu et al., 2015).

Nawawi and Nawi (2014) have produced a new variation of nitrogen doped TiO_2, known as carbon coated nitrogen doped TiO_2, synthesized from Degussa $P25TiO_2$ and urea (carbon and nitrogen precursor) via a mechanical mixing and thermal heating method. This photocatalyst showed the deposition of a carbon graphite layer on the surface of $P25TiO_2$ while the nitrogen atoms were incorporated

into the lattice of P25. This photocatalyst showed efficient photocatalytic degradation of reactive red 4 (RR4), methylene blue and phenol under visible light irradiation (Nawawi and Nawi, 2014).

1.8   Immobilization of photocatalyst

The conventional approach in applying TiO_2 for photocatalytic degradation of organic pollutants is through slurry or suspended system. The application of TiO_2 in suspended modes shows excellent photocatalytic performance, however, it requires expensive post-treatment filtration process to separate the nano-sized TiO_2 photocatalyst from the treated water. This constraint the use of TiO_2 photocatalyst for practical field application Alternatively, the photocatalyst may be applied in an immobilized system on solid supports which eliminates a post-treatment filtration step whereby the immobilized TiO_2 particles can be easily recovered and reused again (Meyer et al., 2004; Nawi and Zain, 2012).

Various immobilized techniques have been reported in the literatures, including dip-coating (Nawi and Zain, 2012), spray-coating (Han et al., 2013), low temperature hydrothermal (Zhang and Yang, 2012) and anodic spark deposition (Meyer et al., 2004) methods. Glass (Hosseini et al., 2007; Miranda-García et al., 2011; Nawi and Zain, 2012), steel (Meyer et al., 2004), perlite granules (Hosseini et al., 2007), polyester fiber (Han et al., 2013) and polyamide fabric (Zhang and Yang, 2012) have been used as support materials for the immobilization of TiO_2. The ideal support material should be transparent to the irradiation, promote contact between pollutants and photocatalyst besides being resistant to the oxidizing conditions. Borosilicate glass is an ideal support material since it is transparent in the range of TiO_2 activity (~300-400 nm); it has excellent photocatalyst adherence to it and

allows high temperature treatment (Miranda-García et al., 2011). The glass-supported TiO_2 also shows the formation of oxygen bridges between OH groups from the supporting glass plate and TiO_2 photocatalyst surface during the thermal treatment, thus a mechanically stable coating is expected from a properly coated TiO_2 on the surface of glass plates (Hosseini et al., 2007).

In general, the photocatalytic activity of a photocatalyst reduces after immobilization. It is due to the decreasing active surface area of the photocatalyst, the introduction of ionic species in the system and difficulty in solution exchange (Rachel et al., 2002). The immobilization of TiO_2 also reduces the accessibility of photocatalyst active surface to photons and pollutants, thus leading to the slower photocatalytic degradation rate. Besides, the decrease in photocatalytic activity after immobilization is due to the loss of some TiO_2 particles from the photocatalyst surface and also by the accumulation of by-products from photocatalytic degradation process at the active site of immobilized TiO_2 (Rao et al., 2004).

Nawi and Zain (2012) reported an immobilized $P25TiO_2$ system having better photocatalytic activity than its slurry mode counterpart in the degradation of methylene blue. This immobilized $P25TiO_2$ system was fabricated using epoxidized natural rubber (ENR-50) and polyvinyl chloride (PVC) as the binders. The negative impact of the reduced surface area was overcome by the photo-etching process where the ENR-50 binder decomposed and produced an immobilized photocatalyst system with higher surface area, bigger pore volume and smaller particle size. In addition, the immobilized photocatalyst showed sustainable photocatalytic efficiency up to 10 cycles of repeated application (Nawi and Zain, 2012).

Despite of the studies reported on the immobilization of TiO_2 photocatalyst, however, not much works had reported the immobilization of nitrogen doped TiO_2.

The immobilization of nitrogen doped TiO_2 is expected to create a photocatalyst system that can degrade the organic pollutant under total visible light and can be repeatedly used. Therefore, it is intended to fabricate immobilized nitrogen doped TiO_2 in this study.

1.9 ENR and PVC polymers

Epoxidized natural rubber (ENR) is a polymer produced by chemical modification of natural rubber with performic acid as shown in Figure 1.4 (Al-Mansob et al., 2014). Although ENR consists of two functional groups that are double bonds and epoxy sites where the cross-linking can occur, however, it still exhibits the properties of natural rubber. ENR with various degrees of epoxidation can be prepared, and the commercially available grades are ENR-25 and ENR-50 which contain 25 and 50 mol% epoxidation, respectively. The epoxidation process of natural rubber enhances the compatibility of ENR with other polymer containing polar groups like polyamide and polyvinyl chloride (PVC) (Pire et al., 2010). ENR can be modified and used in various applications including in tires making, corrosion coating, cosmetic and adhesives. The use of ENR as a polymer matrix in advances composite materials has gained interest due to the presence of epoxy sites, which allow the interaction with a second polymer (Mahmood and Azarian, 2015).
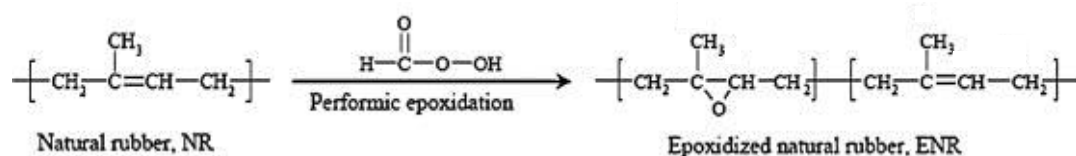
Figure 1.4: Formation of epoxidized natural rubber (Al-Mansob et al., 2014).

Polyvinyl chloride (PVC) is a polar, crystalline polymer and forms the physical polymer gels in solvents (Hong and Huang, 1999). PVC is widely used in

many applications such as children's toys, audio records, credit cards, packaging, bottles, wiring, wallpapers, pipes and in the medical field such as tubing and blood bags (Jia et al., 2015). PVC can be blended with other polymers such as ENR to gain a polymer composite with desired properties. The PVC/ENR blends have the potential to be used as a conveyor belt cover, cable jackets, hose covers and linings, footwear and cellular sporting surfaces. Studies were conducted to enhance the physical and chemical properties of PVC/ENR blends via polymerization and crosslinking reactions (Ratnam and Zaman, 1999a). The previous study reported the formation of crosslinks in PVC/ENR blends using electron beam irradiation. The crosslink of PVC/ENR blends shows improvement in tensile strength, elongation at break, hardness and aging properties of blends. The enhancement in the PVC/ENR blend properties is due to crosslinking of the ENR phase with PVC. The interaction of two different polymers resulted in the improved miscibility of the blends (Ratnam and Zaman, 1999b).

The combination of PVC and photocatalyst semiconductor had also gained interest in recent years. This is due to the capability of PVC to be converted to a conjugated polymer by the heating process at high temperatures, such as at 150 $^{\circ}$C via dehydrochlorination process as shown in Figure 1.5 (Wang et al., 2014).
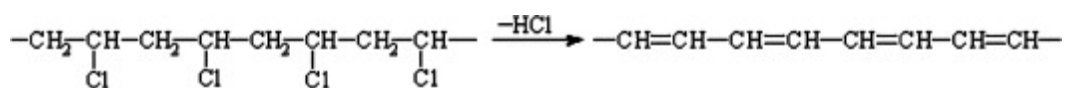
Figure 1.5: Dehydrochlorination process to obtain conjugated polymer from PVC (Wang et al., 2014).

Previous studies showed that the combination of conjugated polymer and semiconductor photocatalysts enhanced the photocatalytic activity of a

semiconductor in visible light regions. Luo et al. (2015) reported the synthesized composite film consisting of conjugated polymer from PVC and tin (IV) dioxide (SnO_2) possess excellent visible-light photo-activity for photocatalytic degradation of rhodamine B. This composite film was prepared by casting the PVC/SnO_2 composite followed by heating at a temperature higher than 150 ^{O}C to obtain conjugated polymer PVC/SnO_2 films (Luo et al., 2015). Wang et al. (2015) have reported that surface modification of cadmium (II) sulfide (CdS) with conjugated polymer derived from PVC shows better photocatalytic activity for photocatalytic degradation of methyl orange and phenol. The presence of conjugated polymer from PVC in the small amount on the surface of CdS did not affect the crystallinity and size of CdS. In fact, it enhanced the absorption of visible light and the separation efficiency of the photo-generated electrons and holes (Wang et al., 2015). Since the conjugated polymer can be produced from PVC with the presence of photocatalyst, the oxidation of PVC can be potentially carried out in situ on the immobilized TiO_2 that utilized PVC as an adhesive.

1.10   Agriculture and pesticides usage

The three major cereals in the agriculture sector are wheat, rice and maize. Wheat is grown all over the world and has become the most important cereal crop in the Northern hemisphere, Australia and New Zealand. Maize is mainly produced in the USA while most of the rice is produced in Asia (Oerke, 2006). Rice is the major staple food for more than 3 billion people worldwide. In Asia, 75 % of rice is produced through the irrigated rice production system, where the rice is grown under continuous flooding or submerged soil conditions. It is estimated that 45 % of total freshwater in Asia is consumed by the rice production sector. However, this sector

may suffer from the diminishing clean water resource for rice irrigation (Tao et al., 2015). In addition, less rice production is also due to the presence of weeds, animal pests and pathogens (Oerke, 2006). In order to increase the crop production, farmers use pesticides (herbicide, fungicide and insecticide) to remove weeds, pests and pathogens from crops.

Generally, the term pesticide is used to represent a wide range of compounds which are commonly classified based on their (i) pesticidal actions such as fungicides, herbicides, insecticides and nematicides, (ii) general chemical nomenclatures such as organochlorides and organophosphate, or (iii) mode of action (McKnight et al., 2015). The worldwide usage of pesticide is roughly about two million tons per year with 45 % being used in Europe, 24 % in the USA and 25 % is applied to the rest of the world (Yadav et al., 2015). The use of pesticides in the agricultural sector successfully enhances the crop production. As time passed, farmers use pesticides in higher concentration, mixing several pesticides together and apply pesticides in higher frequency to further enhance the crop yield (Wilson and Tisdell, 2001). These extreme applications of pesticides may lead to the presence of excess pesticides in the agricultural field. These pesticides are introduced into the soil by missing their intended target, though surface and subsurface runoff from treated plants or by spillage during application. Later, the leaching of pesticides from soil to groundwater aquifers resulted in the polluted groundwater (Yadav et al., 2015).

The negative impact from the excess application of pesticides is extended to human health. Pesticides may impact human health via residential proximity to agricultural pesticide applications, where the pesticides may drift through the air and ground, and through post-application volatilization. The drifting of pesticides affects the surrounding residents and field workers, and may lead to acute symptoms such as

vomiting and breathing problems (VoPham et al., 2015). Another source of pesticide exposure to human is through food chains as some residues of persistent pesticides may remain longer in the targeted crops. Besides, some pesticides are liposoluble compounds and they can accumulate in the fatty parts of animals such as milk, blood and fatty tissue. Humans are exposed to the applied pesticides by consuming food made from the polluted crops and from poultry that are in contact with the polluted soil and water (Yadav et al., 2015). Pesticides represent a major group of endocrine disrupting chemicals and the exposure of pesticides to humans can disrupt the human endocrine system and they have been associated with adverse health effects such as cancer, neurodegenerative disorders and reproductive disorders (Ghisari et al., 2015). Presently, herbicides are commonly used in place of another type of pesticides in developed countries as herbicides have a lower acute or immediate toxicity (Yadav et al., 2015). Herbicides mechanism of action is mainly targeting the photosynthesis pathway while insecticides act by disrupting the function of the nervous system (DeLorenzo et al., 2001). This makes the herbicides to have less negative impact towards human as compared to the insecticides.

In countries such as Malaysia, Philippines, Vietnam and Sri Lanka, rice is cultivated using puddle-transplanted rice and dry-seeded rice systems. Most farmers who practice dry-seeded rice method utilize herbicides for weed control management. The common herbicides used in dry-seeded rice for controlling sedges and broadleaved weeds are sulfonylurea and phenoxy compounds while propanil, acetochlor, fenoxaprop and quinclorac have been extensively used for controlling grass weeds (Awan et al., 2015).

1.11   2,4-Dichlorophenoxyacetic acid (2,4-D)

2,4-dichlorophenoxyacetic acid (2,4-D) is a synthetic auxin herbicide that is widely used to control the growth of broad-leaf weeds. The chemical structure of 2,4-D is shown in Figure 1.6. 2,4-D was first synthesized in the early 1940s and was used to increase the crop production such as wheat, maize, rice and other cereals during World War II (Song, 2014). 2,4-D is the first synthetic auxin analogue of indole-acetic acid herbicide. 2,4-D inhibits the growth of weeds by disturbing the normal growth and development of target plants, provoking lethal damage that leads to uncontrolled cell division. The exposure of targeted plants to 2,4-D leads to the accumulation of reactive oxygen species, disrupting the calcium channels and cell division, creating the defects in the cell wall and membrane before leading to localized cell death (Bhat et al., 2015).
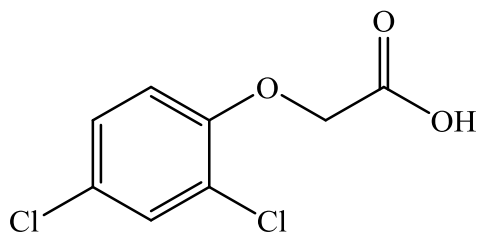
Figure 1.6: Chemical structure of 2,4-dichlorophenoxyacetic acid (2,4-D).

2,4-D becomes the preferable herbicide for the application in agricultural and residential area due to its low cost and good selectivity (Tang et al., 2015). However, the excessive use of 2,4-D for weed control leads to environmental problems since this herbicide might volatilize into air, remain in the soil or runoff into the natural water system (Trillas et al., 1995). With its solubility in water of 900 mg L^{-1} at 25 $^{\circ}$C (Kwan and Chu, 2004) and half-life around 10 days (Bhat et al., 2015), 2,4-D is persistent in the environment. 2,4-D is known as an endocrine disruptor and the exposure of this herbicide to mammalian cells, results in the alteration of the cells

and impairing the cellular function, particularly cells that are related to the central nervous system (Alves et al., 2013).

Since the presence of 2,4-D in the environment leads to the negative impacts towards human and other living creatures, studies have been conducted to remove 2,4-D from the aqueous solutions. Various techniques have been employed for the removal of 2,4-D including adsorption (Ova and Ovez, 2013; Tang et al., 2015), photocatalytic degradation, (Murcia et al., 2015), biological oxidation (Ballesteros Martín et al., 2009), Fenton-like process (Chen et al., 2015) and photocatalytic degradation (Del Ángel-Sanchez et al., 2013; Herrmann et al., 1998; Trillas et al., 1995). Among these methods, photocatalytic degradation is a widely used method to degrade 2,4-D. Several photocatalysts such as bismuth tungstate (Pei and Chu, 2013), zinc oxide (Sherly et al., 2015), iron (Kwan and Chu, 2003), hematite (Jaafarzadeh et al., 2017) and titanium dioxide (Rivera-Utrilla et al., 2012) were used for photocatalytic degradation of 2,4-D with titanium dioxide as the commonly used photocatalyst. In these recent years, modified TiO_2 has been used for photocatalytic degradation of 2,4-D. TiO_2 has been modified with metal such as tin (Rangel-Vázquez et al., 2015), silver (Tang et al., 2012), nickel (Rodríguez et al., 2013) and lanthanum (Siah et al., 2017) to enhance its photocatalytic degradation activity on 2,4-D. Besides, Del Angel-Sanchez et al. (2013) reported the preparation of nitrogen doped TiO_2 using sol-gel and sonochemistry methods. The synthesized photocatalyst successfully degraded 2,4-D herbicide under visible light irradiation (Del Ángel-Sanchez et al., 2013).

Even though the photocatalytic degradation of 2,4-D was extensively studied in the literatures, nevertheless, the photocatalytic degradation of 2,4-D by the immobilized nitrogen doped TiO_2 have not been reported in the study. Besides, the