PHOTOCATALYTIC OXIDATION OF CHITOSAN AND ITS DERIVATIVES AND PHENOL BY IMMOBILIZED TiO_2 BILAYER ASSEMBLAGE SYSTEMS UNDER VISIBLE LIGHT

By

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LIST OF ABBREVIATIONS AND SYMBOLS

a. u.	Arbitrary units
AOPs	Advance oxidation processes
^{13}C-NMR	^{13}C Nuclear Magnetic Resonance
CHN	Carbon, Hydrogen and Nitrogen elemental content
COD	Chemical Oxygen Demand
CS	Chitosan
CS-ECH	Cross-linked chitosan- epichlorohydrin
CS-GLA	Cross-linked chitosan- glutaraldehyde
e^-	Negative electron
e-beam	Electron- beam
E_{bg}	Energy band gap
ECH	Epichlorohydrin
EDX	Energy Dispersive X–ray
FTIR	Fourier-transform infrared spectroscopy
GLA	Glutaraldehyde
h^+	Positive hole
hv	Photonic energy
k_{app}	Apparent (pseudo) first-order rate constant
L-H	Langmuir-Hinshelwood
LR	Leaching ratio
LUMO	lowest unoccupied molecular orbital
NHE	Normal hydrogen electrode
PF	Phenol Formaldehyde resin
PLS	Photoluminescence spectrum
SEM	Scanning Electron Microscopy
SI	Swelling Index
TEM	Transmission Electron Microscopy
TGA	Thermal gravimetric analysis
UV	Ultraviolet
UV-Vis DRS	UV-Visible diffuse reflectance spectroscopy
VB	Valence band
V-UV	Vacuum-ultraviolet
Ω	Ohm

PENGOKSIDAAN PEMFOTOMANGKIN KITOSAN DAN TERBITANNYA DAN FENOL OLEH TiO_2 TERIMOBILASASI MELALUI SISTEM SUSUNAN DUA LAPISAN DIBAWAH SINARAN CAHAYA NAMPAK

ABSTRAK

Sistem dwilapisan mudah yang terdiri daripada TiO_2 sebagai lapisan atas dan kitosan (CS), rangkai silang kitosan-gluteraldehid (CS-GLA) dan kitosan-epiklorohidrin (CS-ECH) sebagai lapisan bawah telah berjaya dihasilkan dan dipegunkan pada plat kaca. Sifat-sifat pemendapan dan kelekatan TiO_2 dapat diperbaiki dengan menambah pengikat organik seperti getah asli terepoksi (ENR_{50}) dan resin fenol-formaldehid (PF) di dalam formulasi penyaduran. Apabila sistem dwilapisan ini melalui proses sinaran di dalam larutan akueus yang diudarakan di bawah 45-W lampu pendarfluor telah menyebabkan perubahan yang ketara terhadap kandungan kedua-dua ENR_{50} dan PF pada lapisan atas TiO_2, selain daripada perubahan fizik-kimia yang istimewa pada lapisan bawah CS, CS-GLA dan CS-ECH. Walau bagaimanapun, telah didapati bahawa semasa fotodegradasi sebahagian daripada ENR_{50} dan PF telah bertindak sebagai agen pembentukan liang untuk menghasilkan bukaan liang pada permukaan TiO_2 seperti yang tunjukkan oleh analisis SEM, sementara analisis TGA, EDX dan ujian COD pula menunjukkan secara kuantitatifnya tiada perubahan yang signifikan terhadap kandungan ENR_{50} dan PF yang boleh didapati selepas 5 kitaran penggunaan berulangan. Struktur berongga lapisan TiO_2 terpegun ini membenarkan penyebaran pencemar dengan lebih efektif, meningkatkan penembusan cahaya dan memperbaiki sifat optik seperti yang ditunjukkan oleh analisis spektroskopi fotopendarcahaya (PLS).

Sementara itu, lapisan bawah CS, CS-GLA dan CS-ECH teroksida secara perlahan dalam 5 kitaran penggunaan berulangan. Kajian pencirian melalui analisis unsur, spektroskopi inframerah transformasi fourier (FT-IR), spektroskopi resonans magnet nukleus keadaan pepejal ^{13}C, spektroskopi pemantulan bauran UV-Sinar nampak (DRS), spektroskopi fotopendarcahaya (PLS) dan ukuran pengembangan secara lazimnya menunjukkan pembentukan kumpulan karbonil dan penyingkiran sebahagian daripada kumpulan amino tanpa mengubah sebahagian besar struktur polimer CS dan terbitan rangkaisilangnya. Dalam semua kes, warna lapisan CS telah dilihat bertukar menjadi lebih keperangan dan pengambilan air telah berkurangan. Pembentukan serentak pembukaan liang pada permukaan TiO_2 dan pengoksidaan lapisan bawah CS, CS-GLA dan CS-ECH bertanggungjawab terhadap pengurangan kadar penggabungan semula pasangan lubang elektron di permukaan lapisan atas TiO_2. Akibatnya, berdasarkan pada pemalar kadar tertib pertama seperti yang diperolehi daripada analisis HPLC, aktiviti pemangkinan foto oleh sistem yang digunakan untuk penyingkiran fenol mematuhi urutan seperti berikut TiO_2/CS-ECH > TiO_2/CS-GLA > TiO_2/CS ≥ rampaian TiO_2 > TiO_2 lapisan tunggal. Perubahan yang sama telah diperolehi untuk kecekapan pemangkinan foto dan kadar mineralisasi bagi fenol dan bahan perantaraannya seperti asid maleik, asid fumarik, hidrokuinon dan katekol. Kesan penjerapan boleh diabaikan dan kesemua sistem terpegun ini boleh diguna semula untuk sekurang-kurangnya 10 kitaran tanpa kehilangan keaktifannya.

PHOTOCATALYTIC OXIDATION OF CHITOSAN AND ITS DERIVATIVES AND PHENOL BY IMMOBILIZED TiO_2 BILAYER ASSEMBLAGE SYSTEMS UNDER VISIBLE LIGHT

ABSTRACT

Simple bilayer systems consisting of TiO_2 as a top layer and chitosan (CS), cross-linked chitosan-glutaraldehyde (CS-GLA) and chitosan-epichlorohydrin (CS-ECH) as sub-layers were successfully fabricated and immobilized onto a glass plate. The deposition and adhesive properties of TiO_2 were improved by adding organic binders like epoxidized natural rubber (ENR_{50}) and phenol-formaldehyde resin (PF) in the coating formulation. Exposing these bilayer systems in aerated aqueous solution to 45-W fluorescent lamp caused significant changes in content of both ENR_{50} and PF of TiO_2 top layer, in addition to the remarkable physico-chemical changes of CS, CS-GLA and CS-ECH sub-layers. However, it was found that the ENR_{50} and PF had actually acted as pore-forming agents via their photodegradation process to create macro pores on the TiO_2 surface as shown by SEM analysis, while TGA, EDX and COD analyses indicated quantitatively that there is no significant change in ENR_{50} and PF content that can be observed after 5 cycles of repeated usage. This porous structure of immobilized TiO_2 layer allows better diffusion of pollutants, increases the light penetration and improves the optical property as indicated by photoluminescence spectroscopy (PLS) analysis.

CS, CS-GLA and CS-ECH sub-layers were mildly oxidized within 5 cycles (Each cycle was equivalent to two hours of irradiation) of repeated usage. Characterization studies via elemental analysis, Fourier-transform infrared spectroscopy (FTIR), ^{13}C solid state nuclear magnetic resonance (^{13}C-NMR), UV-

Visible diffuse reflectance spectroscopy (DRS), photoluminescence spectroscopy (PLS) analyses and swelling measurement generally indicated the formation of carbonyl group and partial elimination of some amino groups without altering much of the whole polymeric structure of CS and its cross-linked derivatives. In all cases, the visual color of sub-layers of CS and its cross-linked derivatives had converted to more intense brown and less water uptake was also observed. The simultaneous generation of macro pores on TiO_2 surface and oxidation of CS, CS-GLA and CS-ECH sub-layers are responsible for the reduction in the recombination rate of electron-hole pair on the surface of TiO_2 top layer. Consequently, according to the pseudo first-order rate constant as determined by HPLC analysis shows that the photocatalytic activity of applied systems for phenol removal followed this order TiO_2/CS-ECH > TiO_2/CS-GLA > TiO_2/CS ≥ TiO_2 in slurry > TiO_2 single layer. The same trend was observed for photocatalytic efficiency and mineralization rate for phenol and its intermediates, which were identified to be maleic acid, fumaric acid, hydroquinone and catechol. In fact, the effect of adsorption was extremely negligible and all these immobilized systems were reusable at least for up to 10 cycles of applications without losing their photocatalytic activity.

CHAPTER ONE

INTRODUCTION

1.1 Photocatalysis

The phenomenon of photocatalysis can be defined as the combination of photochemistry and catalysis. More precisely, the meaning of “photocatalysis” herein implies direct interaction between the light and catalyst (Hamal and Klabunde, 2007). Therefore, there is no photoreaction on illumination with light alone. Thus, reaction usually demands the use of photocatalyst which implies that the photon assists the generation of catalytically active species (Chatterjee and Dasgupta, 2005).

However, all the knowledge that was acquired during the development of semiconductor photoelectrochemistry during 1970 and 1980s had significantly enhanced the development of photocatalysis (Heller, 1981). The application of photocatalysis, especially photocatalysis using semiconductor particles, is an emerging new scientific technology. This is especially true after the discovery by Fujishima and Honda of the photolysis of water into environmentally clean fuels (hydrogen and oxygen) utilizing an electrode of titanium dioxide (TiO_2) in an electrochemical cell (Fujishima and Honda, 1972). Following this, several works have been devoted solely towards understanding the essential concept of the photocatalysis process for enhancing the photocatalytic efficiency as well as investigating the overall advantages of the photocatalytic process for the environmental remediation technologies. Hence, several advantages can be concluded from applying this technology in environmental protection, which are listed as follows (Kabra et al., 2004):

a. Photocatalysis exhibits an alternative way for the energy-intensive traditional treatment methods with great capability of harvesting renewable and pollution- free solar energy.

b. Photocatalysis technology does not require transformation of treated pollutants from one medium to another, unlike conventional treatments methods.

c. High capability for destroying a wide range of hazardous compounds in different wastewater streams.

d. Potentially applicable to aqueous and gaseous-phase treatment, as well as to some extent solid (soil) phase treatments.

e. The photo-reaction conditions for photocatalysis in general are mild, the photodegradation time is modest, and less chemical agents input are required.

f. The generated intermediates of treated hazardous compounds are minimal.

g. The photocatalyst (semiconductor) powder is recoverable and reusable for many cycles of treatment.

1.2 Fundamental mechanism of photocatalysis

Unlike metals which already have a continuum of electronic state, semiconductors posses a void energy region without energy levels that are available to promote the recombination of an electron and hole generated by photoactivation in the solid semiconductors. The void region that centered between the top of the filled valence band (VB) and the bottom of the vacant conduction band (CB) is called energy band gap (E_{bg}) (Linsebigler et al., 1995). The process of semiconductors photocatalysis basically includes the following steps. If the energy of the incident photon is equal or exceed the band gap energy (E_{bg}) of the semiconductors/

photocatalyst, absorption of the photonic energy (hυ) by the semiconducting solids leads to excitation of an electeron (e^-) from the valence band to the conduction band of the semiconductor and a positive hole (h^+) would be left in the valence band. Ultraviolet (UV) or near-UV photons are typically needed for this type of photoreaction (Mills and Hunte, 1997).

$$Semiconductor \xrightarrow{h\upsilon \geq E_{bg}} h^+ + e^- \qquad (1.1)$$

Thus, the generated pair (e^--h^+) immediately migrates to the semiconductor/photocatalyst surface where they either recombine, producing wasted-thermal energy or take place in subsequent reduction and oxidation (redox) processes with any compound, which might be adsorbed on the photocatalyst surface to give the necessary end-products (Chatterjee and Dasgupta, 2005; Kabra et al., 2004). The overall mechanism of the photo-induced semiconductor/photocatalyst is illustrated in Figure 1.1 (Mills and Hunte, 1997).

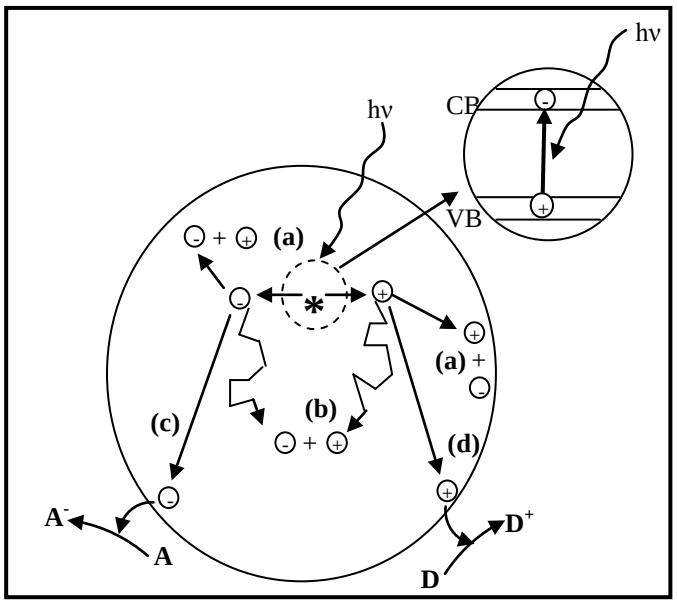

Figure 1.1: Illustration of the main processes occurring on a semiconductor particle following the electronic excitation. Electron-hole pair recombination can occur at the surface (reaction (a)) or in the bulk (reaction (b)) of the semiconductors. At the surface of the particle, photogenerated electrons can reduce an electron accepter A (reaction (c)) and photogenerated holes can oxidize an electron donor D (reaction (d)). The combination of reaction (c) and (d) presents the semiconductor sensitization of the general redox reactions (Mills and Hunte, 1997).

Several types of semiconductor catalyst such as TiO_2, ZnO, ZnS, CdS, Fe_2O_3 and GaP have been tested as photocatalysts for the degradation of a wide range of ambiguous refractory organic pollutants into harmless biodegradable compounds, and finally mineralize them to CO_2, H_2O and other mineral acids. Among all of the semiconductors catalysts, titanium dioxide, TiO_2, is close to being an ideal bench mark photocatalyst in the environmental photocatalysis applications (Chong et al., 2010).

The various applications of TiO_2 in the photocatalysis technology include selective synthesis of organic compound (Pillai and Endalkachew, 2002), photokilling of pathogenic organism (Sichel et al., 2007), cancer treatment (Fujishima et al., 2000), self-cleaning and anti-fogging (Fujishima and Zhang, 2006), air cleaning (Sun et al., 2003), detoxification and remediation of water (Dominguez et al., 2005), degradation of hazardous inorganic compounds (Kim et al., 1998), decontamination of soil (Hamerski et al., 1999) and treatment of heavy metals (Eliet and Bidoglio, 1998). In addition to the unique characteristic of TiO_2 in the wide range of applications mentioned above, it also offers unlimited applications by the presence of photoinduced phenomenon which is depicted in Figure 1.2 (Carp et al., 2004).

1.3 TiO_2 as semiconductor photocatalyst

1.3.1 General remarks of TiO_2

Titanium dioxide (TiO_2) is one of the members of transition metal oxides. In the beginning of the 20th century, titanium dioxide was used intensively in industrial products in order to replace the older toxic lead oxides as pigments for white paint. Recently, the yearly production of TiO_2 passed 4 million tons. This pigment has been

widely used in various applications involving paint, plastics, rubber, inks, papers and textile, in addition to the considerable amount of the global production used in food and pharmaceuticals products (Carp et al., 2004).

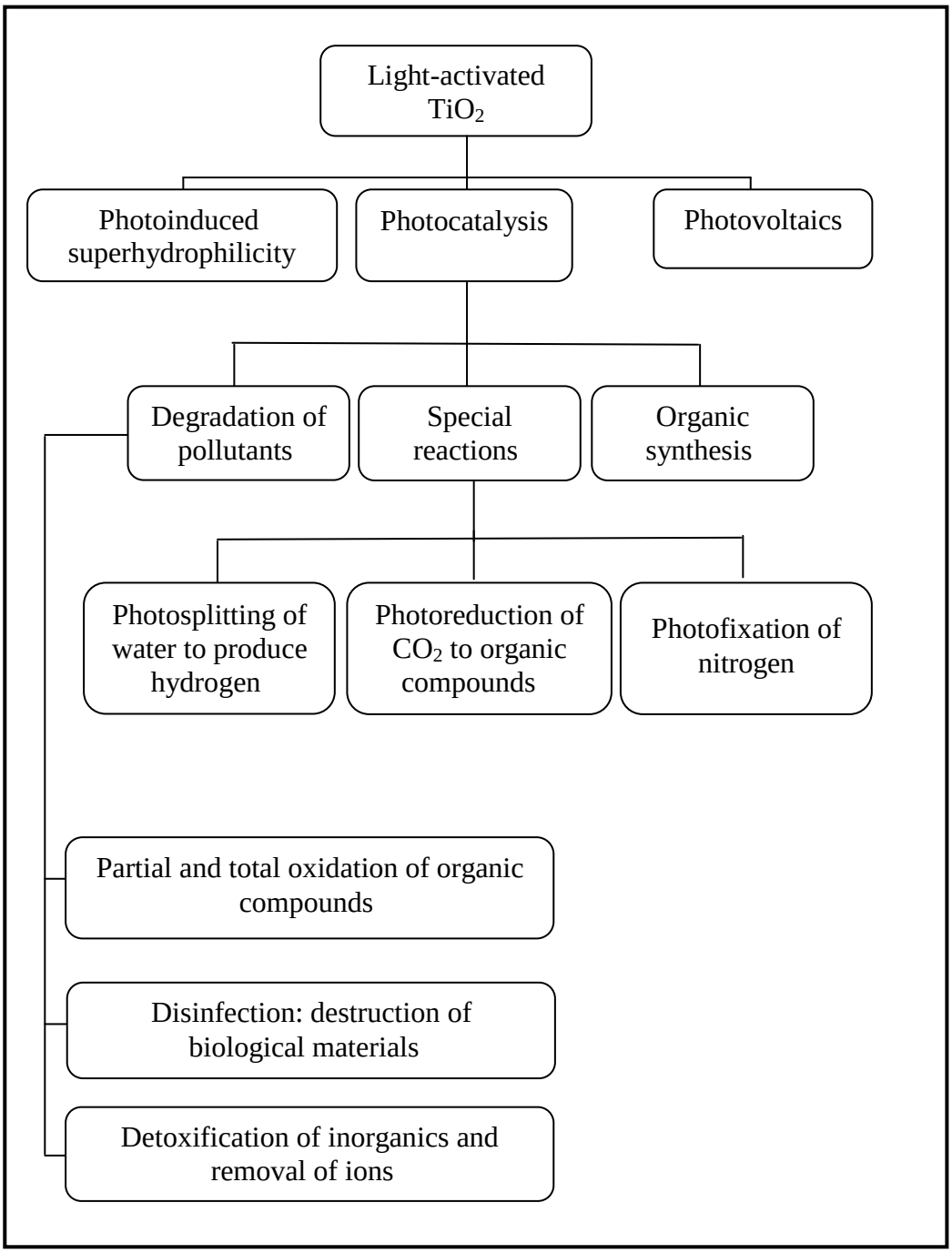

Figure 1.2: Photoinduced processes on TiO_2 (Carp et al., 2004).

In fact, there are two possible ways to manufacture the commercial TiO_2 pigments, either by sulfate or chloride processes. The sulfate process involves direct reaction between the TiO_2 ore and sulfuric acid; then the product is hydrolyzed to produce a hydrate oxide, which is followed by calcination process at 900 ^oC to obtain pigmentary TiO_2 (Delgado-Vargas and Paredes-Lopez, 2003). The chloride process was improved in 1920 but not commercially applicable until the late 1950s. In this process, TiO_2 ore reacts with gaseous chlorine in the presence of coke to produce liquid titanium tetrachloride. The product is distilled and oxidized in the vapor phase to obtain pigmentary TiO_2 (Blakey and Hall, 1988).

1.3.2 Crystallographic structure of TiO_2

In nature, TiO_2 crystallizes in three crystalline forms: anatase (its name is derived from the Greek word 'anatasis' meaning 'extension'), rutile (its name is derived from the Latin word 'rutilus' meaning 'red') and brookite (its name is named in honor of the English mineralogist, H.J. Brooke). These crystal structures are classified based on the TiO_2^{6-} octahedral unit (Carp et al., 2004).

However, anatase type TiO_2 has a crystalline structure that matches the tetragonal system (with dipyramidal habit) and is employed basically as a photocatalyst in UV light region. The rutile type TiO_2 has a tetrahedral symmetry structure (with prismatic habit) which is mainly utilized as whitening pigment of paint. As for brookite type TiO_2, it has an orthorhombic crystalline structure. All the crystalline forms of TiO_2 are depicted in Figure 1.3 (Bokhimia et al., 2001).

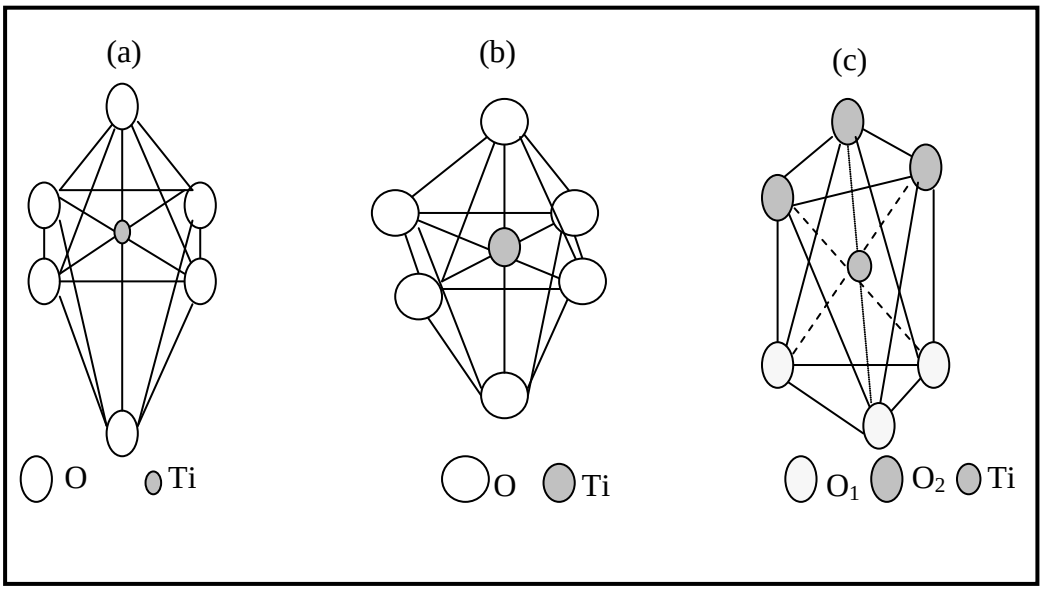

Figure 1.3: Crystal structures of (a) anatase, (b) rutile (b), and (c) brookite (Bokhimia et al., 2001).

1.4 Heterogeneous TiO_2 photocatalysis

Among many different types of advanced oxidation processes (AOPs) are UV, VUV, O_3/UV, O_3/V-UV, H_2O_2/UV, Fenton (Fe^{2+}/H_2O_2), Fenton-like (Fe^{3+}/H_2O_2), photo-Fenton reactions and heterogeneous photocatalysis TiO_2/UV, $TiO_2/UV/H_2O_2$ and$TiO_2/UV/O_3$ (Dominguez et al., 2005). Heterogeneous photocatalyst using TiO_2 as one of the advance oxidation processes (AOPs) has received great attention from the environmental standpoint in comparison with other AOPs as well as the conventional wastewater technologies. The conventional and AOPs technologies are summarized in Figure 1.4 (Chen et al., 2000). However, the heterogeneous photocatalyst is potentially applicable for destruction of a wide spectrum of organic and inorganic water contaminants at ambient pressure and temperature in a relatively short time period without production of polycyclic products. It is also capable of oxidizing pollutants in ppb ranges and only requires oxygen as an oxidizing agent (Carp et al., 2004).

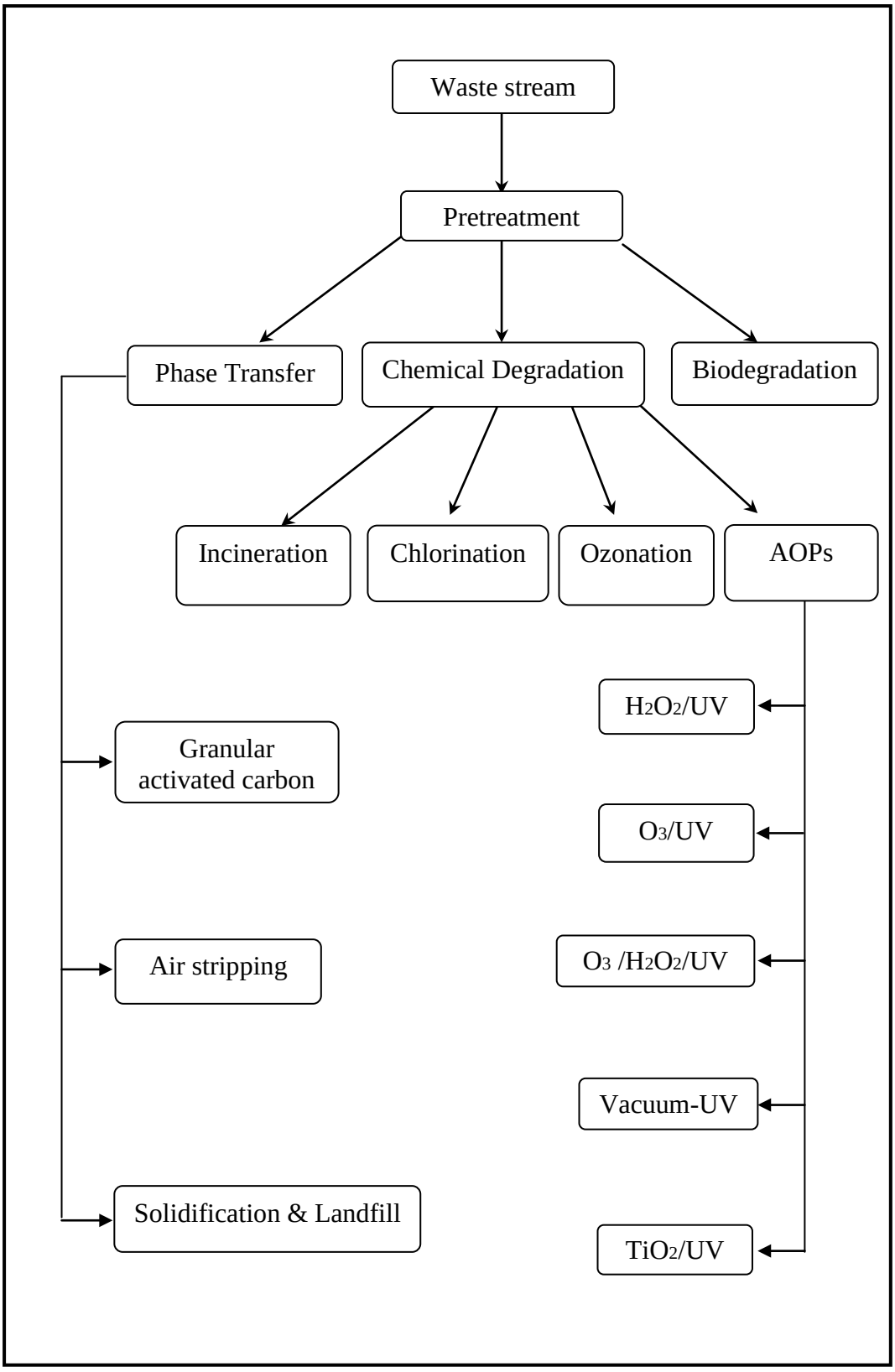

Figure 1.4: Various wastewater treatment technologies in environmental engineering (Chen et al., 2000).

As generally observed, TiO_2 is close to being an ideal photocatalyst and well-researched material in the environmental photocatalysis applications because of its many desirable properties such as follows (Mills and Hunte, 1997):

a. Inexpensive and readily available.

b. Biologically and chemically inert.

c. Having broad spectral absorption response in the UV-C (220-290 nm), UV-B (290-320 nm) and UV-A (320-400 nm) with high absorption coefficient.

d. Photoactive.

e. Photostable (i.e. not liable to photoanodic corrosion for instance).

The process of photocatalytic reaction by TiO_2 takes place by the absorption of ultraviolet (UV) or near-ultraviolet photons ($h\upsilon$) that is equal or exceed the band gap energy (E_{bg}) value for anatase 3.2 eV, or 3.0 eV for rutile onto its surface. An electron would be photoexcited from the valence band (VB) to the empty conduction band (CB) of the TiO_2 and a positive hole would be left in the valence band in femtoseconds. Subsequently, a series of reductive and oxidative reactions will be induced on the TiO_2 surface. The overall mechanism of the electron-hole pair formation as well as the redox reactions involving various compounds adsorbed on the photocatalyst surface when TiO_2 is irradiated with adequate $h\upsilon$ is depicted in Figure 1.5 (Chong et al., 2010). The series of chain oxidative-reductive reactions (Equations (1.2) – (1.12)) that take place at the photoinduced TiO_2 surface was generally proposed as follows (Chong et al., 2010):

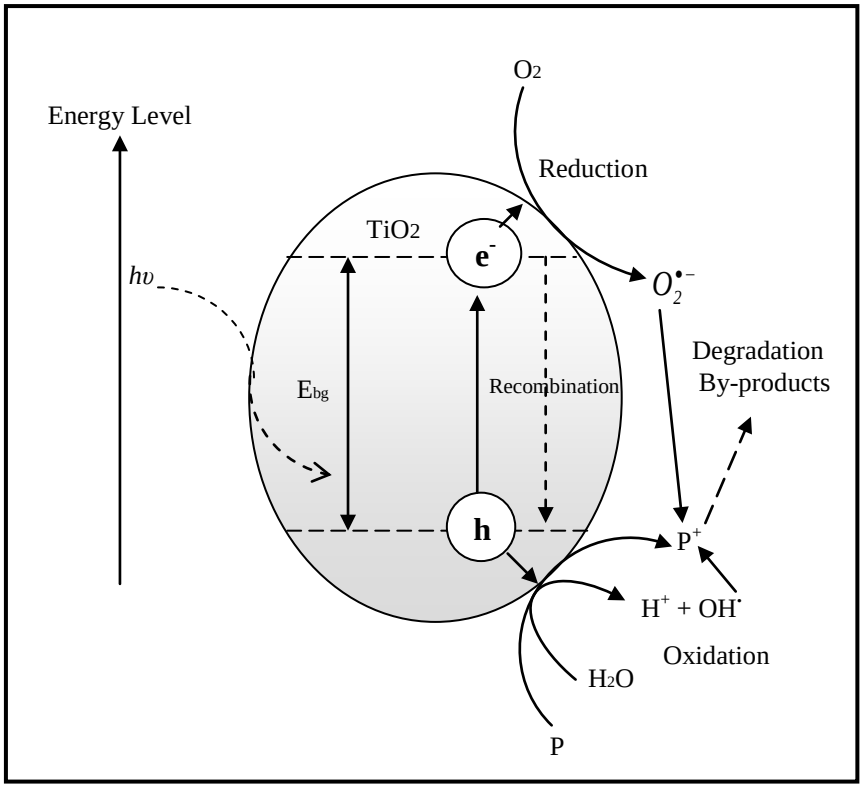

Figure 1.5: Illustration of the photo-induced formation mechanism of electron-hole pair in a semiconductor TiO_2 particle with the presence of water pollutant (P) and dissolved oxygen (Chong et al., 2010).

Photoexcitation :

$$TiO_2 + h\upsilon \rightarrow e^- + h^+ \qquad (1.2)$$

Charge-carrier trapping of e^- :

$$e^-_{CB} \rightarrow e^-_{TR} \qquad (1.3)$$

Charge-carrier trapping of h^+ :

$$h^+_{VB} \rightarrow h^+_{TR} \qquad (1.4)$$

Electron-hole recombination:

$$e^-_{TR} + h^+_{VB}(h^+_{TR}) \rightarrow e^-_{CB} + \text{heat} \qquad (1.5)$$

Photoexcited e- scavenging:

$$(O_2)_{ads} + e^- \rightarrow O_2^{\bullet -} \quad (1.6)$$

Oxidation of hydroxyls:

$$OH^- + h^+ \rightarrow OH^{\bullet} \quad (1.7)$$

Photodegradation by $OH^{\bullet}$:

$$R\text{-}H + OH^{\bullet} \rightarrow \acute{R}^{\bullet} + H_2O \quad (1.8)$$

Direct photoholes:

$$R + h^+ \rightarrow R^{+\cdot} \rightarrow \text{Intermediate (s)/Final Degradation Products} \quad (1.9)$$

Protonation of superoxides:

$$O_2^{\bullet -} + OH^{\bullet} \rightarrow HOO^{\bullet} \quad (1.10)$$

Co-scavenging of e^- :

$$HOO^{\bullet} + e^- \rightarrow HO_2^- \quad (1.11)$$

Formation of H_2O_2 :

$$HOO^- + H^+ \rightarrow H_2O_2 \quad (1.12)$$

The e_{TR}^- and h_{TR}^+ in Equation 1.4 represent the surface trapped valence band electron and conduction band hole respectively. In this regard, it was found that these trapped carriers are usually bound to the TiO_2 surface and do not recombine immediately after photo excitation (Furube et al., 2001). The absence of the electron scavengers leads to direct recombination between the photoexcited electron and the valence band hole in nanosecond with simultaneous release of heat energy (Equation 1.5). On the other hand, the presence of electron scavengers like oxygen is important for prolonging the recombination rate and successful functioning of

photocatalytic performance. Equation 1.6 shows how necessary the presence of oxygen is in preventing the direct recombination of electron-hole pair, while allowing the formation of superoxides radical ($O_2^{\bullet -}$). This $O_2^{\bullet -}$ radical would be further protonated to produce the hydroperoxyl radical ($HO_2^{\bullet}$) and subsequently producing hydrogen peroxide (H_2O_2) as presented in Equations 1.10 and 1.11 respectively.

However, all these occurrences in photocatalysis reactions are dependant totally on the presence of both dissolved oxygen and water molecules. In fact, without the presence of water molecules, the highly reactive hydroxyl radicals ($OH^{\bullet}$) could not be generated and impede the photocatalytic reaction of liquid phase organic pollutants (Chong et al., 2010). In other words, the fundamental task of the heterogenous photocatalyst is to generate free radicals in the solution, mainly the highly reactive hydroxyl radical ($OH^{\bullet}$), which is traditionally responsible for oxidizing almost all organic pollutants to CO_2, H_2O and simple mineral acids because of its high standard reduction potential of 2.8 V vs. NHE, being exceeded only by fluorine (Carp et al., 2004). Thus, during the heterogeneous photocatalytic reactions, the dissolved organic pollutants are degraded to its corresponding intermediates and subsequently mineralized to carbon dioxide and water, if the photo-treatment time is extended (Equation 1.13) (Chong et al., 2010).

$$\text{Organic Contaminants} \xrightarrow{TiO_2/h\upsilon} \text{Intermediate(s)} \rightarrow CO_2 + H_2O \qquad (1.13)$$

The overall photocatalysis reaction as depicted by Equation 1.13 can be divided into five individual steps, which are depicted in Figure 1.6 and detailed out as follows (Fogler, 1999):

a. Movement of the organic pollutant(s) (e.g. A) from the aqueous solution to the TiO_2 surface.

b. Adsorption process of the organic pollutant(s) onto the photoinduced TiO_2 surface (i.e. surface activation by absorption photonic energy occurs simultaneously in this step).

c. Photocatalysis reaction for the adsorbed phase of organic pollutant(s) on the TiO_2 surface (e.g. $A \rightarrow B$).

d. Desorption of the intermediate(s) (e.g. B) from the TiO_2 surface.

e. Movement of the intermediate(s) (e.g. B) from the interface region to the bulk fluid.

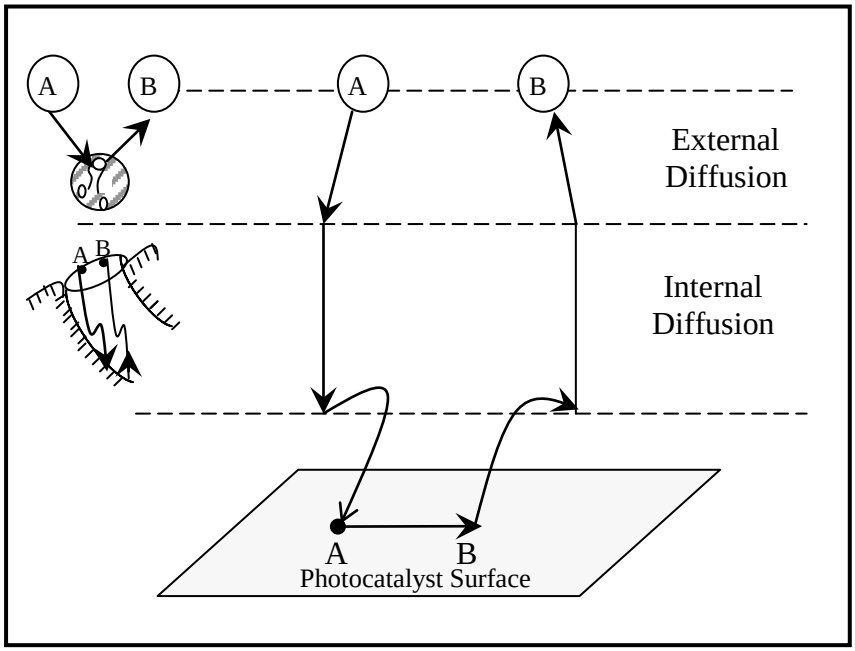

Figure 1.6: Basic steps that occur on the photocatalytic surface in heterogeneous catalytic reaction (Fogler, 1999).

However, it must be noted that the anatase form is the most active allotropic form. For instance, rutile is thermodynamically more stable than anatase, but anatase formation is kinetically preferable at temperature conditions lower than 600 ^{o}C.

Consequently, this lower temperature could offer higher surface area and higher surface density of active sites for pollutants adsorption and for catalytic process (Herrmann, 1999). In fact, rutile type TiO_2 possess a relatively lower band gap energy value of 3.0 eV as opposed to 3.2 eV for anatase and the spectral absorption response of light can also extend to the visible light region, but anatase TiO_2 shows better photocatalytic performance with maximum quantum yield better than the rutile TiO_2 due to its conduction band position which demonstrates stronger reduction power as compared to the rutile TiO_2 (Puma et al., 2008).

In spite of the various advantages obtained from photocatalysis based on TiO_2, heterogeneous photocatalysis for water treatment is still in the developmental stages as some significant challenges remain to be solved before effective applications can even be contemplated. Thus, in order to develop this technology into a cost-effective treatment and as a viable alternative to the current technologies, more fundamental research is needed in order to broaden the spectral response of TiO_2 to visible or solar spectrum and also to solve the post-treatment catalyst powder recovery (Chong et al., 2010).

1.5 Immobilization of TiO_2 photocatalyst

In heterogeneous photocatalyst technology, there are two major designs of heterogeneous photoreactor systems, one in which the TiO_2 powder is used in the suspension or slurry mode and another in which it is immobilized on an appropriate solid support or on the inner wall of a photoreactor. The majority of the early photoreactors have used TiO_2 powder suspended in contaminated water, since it presents high surface area for the photocatalytic reaction to take place and provides almost no mass transfer limitation (Damodar and Swaminathan, 2008).

In fact, the slurry systems normally pose several practical problems of post-treatment catalyst recovering step. This final step is normally a very difficult, costly, energy and time consuming process. The TiO_2 suspended particles have great tendency to aggregate especially at high concentrations. The particles may also cause the scattering of incident UV light resulting in serious difficulty in applying it to the continuous flow system (Andronic and Duta, 2008; Zhang et al., 2007).

Thus, immobilization of TiO_2 powder on solid supports is an alternative and convenient method to solve these problems. Even though the photocatalytic efficiency of the immobilized TiO_2 system may be less than that of the slurry system due to the reduced surface area accessible for photocatalytic reaction as well as low porosity of the supported catalyst layer (Mascolo et al., 2007), but the catalyst can be used for long-term applications without lowering much of its photocatalytic efficiency (Dionysiou et al., 2000; Fabiyi and Skelton, 2000). The summary of some of the supporting materials as well as some deposition methods that are reported in the literatures are shown in Table 1.1.

In order to avoid the cracking and fast peeling off of catalyst layer after short period of usage (Gelover et al., 2004), various deliberate steps should be taken into account in a careful selection of the catalyst deposition parameters that may yield high quality immobilized catalyst in terms of high adhesion properties, and high photocatalytic performance due to high porosity of the immobilized catalyst surface (Andronic and Duta, 2008). The catalyst support should be chemically inert in order to avoid any additional source of water pollution coming from the leaching of the metals ions into the treated solution, in case of using metal substrates as the supporting materials. The same environmental problems would be faced when inorganic adhesives are used as binders for the photocatalyst powder.

Table 1.1 Photocatalytic processes of immobilized TiO_2 under UV light

References	Pollutant degraded	Deposition method	Support material
Uddin et al., 2007	Methylene blue	Sol-gel	Cellulose fiber
Tryba, 2008	Phenol	Manual pasted with a brush	Cotton material
Andronic and Duta, 2008	Methyl orange	Doctor blade	Microscopy glass substrate
Zhang et al., 2007	Phenol	Vapor hydrolysis method	Tetrapod-like ZnO
Tasbihi et al., 2007	Phenol	Sol-gel	Glass beads, silica gel, and quartz sand
Nikolaki et al., 2006	1,3-dichloro-2-propanol	Spray technique using pippeting	Reactor tubular wall
Horikoshi et al., 2002	Nonylphenol polyethoxylate surfactant	Dip-coating	Fiberglass cloth
Chen and Dionysiou, 2006	4-chlorobenzoic acid	Modified sol–gel	Stainless steel
Li et al., 2008	Methyl orange	Dropping TiO_2 solution onto zeolite	Zeolite
Hosseini et al., 2007	Phenol	Direct mixing	Perlite
Kansal et al., 2008	Lignin	Spray gun	Pumice stone
Chen et al., 2006	Benzene	Plasma sprayed	Aluminum
Fabiyi and Skelton, 2000	Methylene blue	Thermal treatment	Polystyrene beads
Watts and Cooper, 2008	4-chorophenol	Direct mixing	Concrete surfaces

Table 1.1: Continued

Damodar and Swaminathan, 2008	Azo dye	Smooth paint brush	PVC tube
Yao et al., 2010	Phenol and methyl orange	Sol–gel-adsorption	Activated carbon
Mascolo et al., 2007	Methyl red	Rotary evaporating	Cylindrical glass
Kim et al., 2005	S. choleraesuis subsp	Drop into catalyst formulation	Chitosan beads
Wang et al., 2002	Trichloroethane	Chemical vapor deposition (CVD)	Pyrex glass tube
Dionysiou et al., 2000	Chlorinated phenols and pesticides	Sol-gel	Stainless steel rotating disk
Fretwell and Doglas, 2001	4-Chlorophenol	Dip or spin-coating	Quartz or glass
Brezova et al., 1997	Phenol	Sol-gel	Glass fibers

1.6 Organic binders

1.6.1 Epoxidized natural rubber (ENR)

Natural rubber (NR) has been commonly used as an economic adhesive material for various products such as tires, products under the car bonnet, gloves, balloons, rubber bands, ets, due to its unique physico-chemical characteristics such as elasticity, stickiness and resilience. However, the great limitations of NR is due to its chemical structure (cis 1,4-polyisoprene) as shown in Figure 1.7, which exhibits low stability to heat, sunlight and oxygen (Yoksan, 2008). The chemical modification of NR is one of the promising ways to modify a part of the carbon-carbon double bonds on the molecular structure of NR into the polar epoxy group and eventually producing epoxidized natural rubber (ENR). The epoxidation process

leads to the reduction of the molecular weight of NR with an increase in the density of the ENR produced. The resultant ENR offers excellent air impermeability, oil and organic solvent proof, wet road grip performance and wide spread applications (Yoksan, 2008; Yu et al., 2008). In general, the preparation of ENR is usually performed by the epoxidation of NR with peracetic, perbenzoic and perpthallic acids in solution (Hong and Chan, 2004). However, the epoxidation process utilizes an in-situ technique based on hydrogen peroxide and formic acid in order to epoxidize NR latex. The preparation steps are depicted in Figure 1.7 (Yoksan, 2008). The Malaysian Rubber Board presently provides two types of ENR, which are namely ENR_{25} and ENR_{50}. The number in each of their name indicates the degree of epoxidation with 25 and 50 mol % of epoxide group's in the ENR molecules. Thus, the properties of glass transition temperature (T_g), oil resistance and melt viscosity increased when the epoxide content of ENR increased as well (Thongnuanchan et al., 2007).

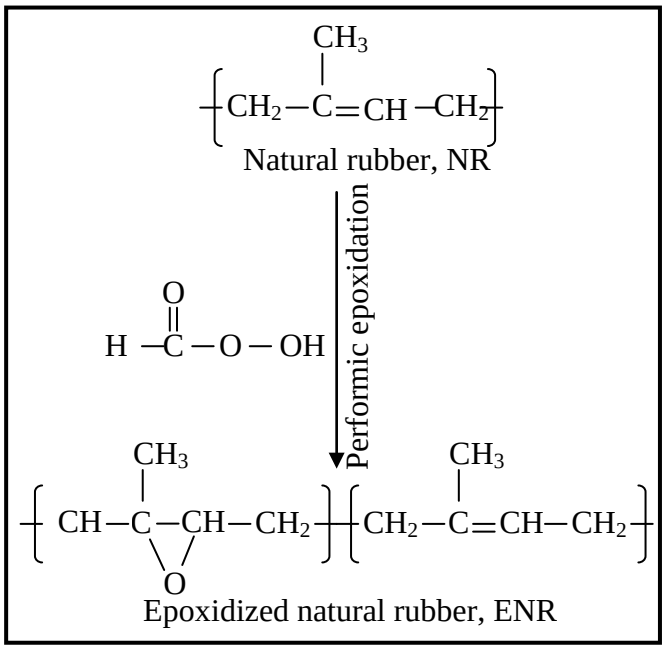

Figure 1.7: Preparation of ENR by performic epoxidation (Yoksan, 2008).

In heterogeneous photocatalyst technology, ENR_{50} had been successfully used as a good emulsifier with PVC in order to improve the distribution of catalyst in the coating formulation and therefore, enhancing the coating properties of TiO_2 photocatalyst on the solid substrate for the photocatalytic degradation of methylene blue (Shin, 2010). Furthermore, ENR_{50} had also acted as adhesives to strengthen the coating conditions of the immobilized TiO_2 in the presence of phenol-formaldehyde resin on various solid supports for photocatalytic degradation of methylene blue and cibacron brilliant red dyes (Amar, 2006). Finally, addition of ENR_{50} into immobilizing solution had improved the adhesiveness and robustness of the coated TiO_2 as well as significantly speeded up the immobilization process of TiO_2 on the aluminum plate by electrophoretic deposition technique for the photocatalytic degradation of phenol (Nawi et al., 2003).

1.6.2 Phenol-formaldehyde (PF) resin

Phenol-formaldehyde (PF) resin is one of the oldest synthetic polymers synthesized in 1907 from the chemical reaction of phenol with formaldehyde. It is also considered the first true thermosetting synthetic polymer and presents many desirable properties such as the resistance of heat, corrosion, wear and the excellent mechanics adhesive capacity (Wanga et al., 2009). However, there are mainly two types of phenol-formaldehyde resins that had been synthesized with different formaldehyde/phenol ratios, namely Novolac and Resol. The phenolic resin composition depends on monomer ratio, catalyst, reaction conditions, and residual free monomers. Furthermore, the temperature and pH conditions play a significant role in the reaction of phenols with formaldehyde and eventually determine the profile and characteristics of the Novolac or Resol resin. Thus, phenol-formaldehyde

resin of novolac type is produced in acidic pH whereas Resol type is produced in alkaline conditions with an excess molar ratio of formaldehyde (1< formaldehyde/phenol < 3) (Poljansek and Krajnc, 2005). The Novolac resin is a linear chain condensation product, which normally produces a nonporous dense layer. The typical chemical structure of novolac phenol-formaldehyde resin is depicted in Figure 1.8 (Wei et al., 2007). In recent years, huge amounts of PF has been consumed in the wood industry in USA, Japan, China and some European countries due to its high bonding strength, excellent water resistance and chemical stability (Jin et al., 2010). Moreover, a combination of PF and ENR_{50} proved to be an excellent coating formulation of TiO_2 powder in heterogeneous photocatalyst technology (Amar, 2006).

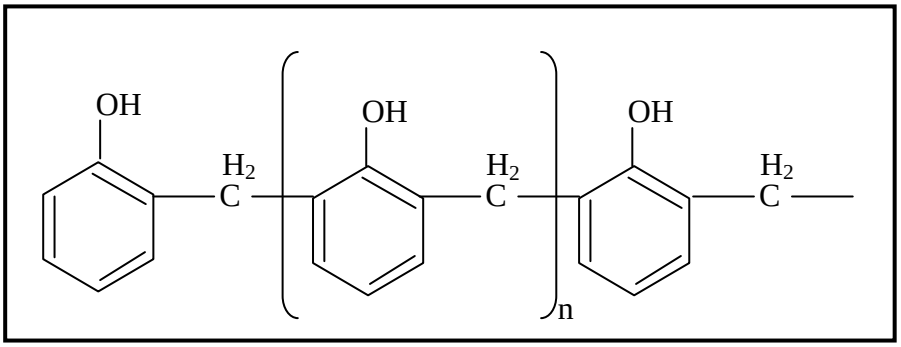

Figure 1.8: Chemical structure of Novolac phenol-formaldehyde resins (Wei et al., 2007).

1.7 Modification of TiO_2 by conventional methods

Several attempts have been made in order to solve one of the major challenges related to the relatively wide band gap of TiO_2 which absorbs only 3-4 % energy of the solar spectrum and restricts its applications due to the need of an UV excitation source (Hamal and Klabunde, 2007). Therefore, further development of

TiO_2 should consider meeting the requirements of large-scale applications of TiO_2 by harvesting more solar energy or increasing its spectral sensitivity towards visible light region. Enhancing the photocatalytic performance of the TiO_2 has been achieved by several conventional approaches as discussed below.

1.7.1 Self-sensitization by using colored pollutants

Organic dyestuffs with visible light absorbing chromophores are responsible for photosensitizing TiO_2 photocatalyst in the field of treating textile wastewater. By this means, the irradiation of adsorbed dye on the TiO_2 surface by visible light leads to the ejection of an electron from the photo-excited dye to the conduction band of TiO_2 photocatalyst. Consequently, the presence of electron scavengers like oxygen leads to the formation of superoxide radical anion, which attacks the dye repeatedly to mineralize it to non-toxic harmless end product(s) (Bauer et al., 2001). The disadvantages of this method come from its limitation for the dyestuff or textile dyes only. The photocatalytic activity that depends basically on the adsorption rate of dyes which is an irreversible process that could cause blocking of the active sites on the catalyst surface and higher photocatalytic performance that demands for the nano-scale TiO_2 particles (Nagaveni et al., 2004).

1.7.2 Dyes modifying TiO_2

Dye sensitization approach depends basically on the anchoring of pigments on the surface of TiO_2 photocatalyst which follows the same concept of self-sensitization mentioned in Section 1.7.1. The high photocatalytic performance of the modified TiO_2 photocatalyst is attributed to the photoinjection of an electron from the conduction band of the excited pigment anchored on the photocatalyst particles to

the conduction band of the TiO_2 support. Consequently, the quantum yield of the redox process would be increased due to the additional formation of superoxides radical $O_2^{\bullet -}$ generated on the TiO_2 conduction band (Iliev, 2002). However, the photocatalytic efficiency of the dyes doping system to the TiO_2 photocatalyst depends on many factors such as the conduction band edge of the semiconductor, the LUMO (lowest unoccupied molecular orbital) of the dye, population of the low lying ligand fields, and the presence of the adsorbates such as water vapor and oxygen (Ozcan et al., 2007).

1.7.3 Doping of TiO_2 with metal ions

Doping of TiO_2 lattice with a series of metal ions such as V, Cr, Mn, Fe, Ni, etc., causes a red shift in the absorption pattern of TiO_2 photocatalyst. This phenomenon is basically due to the creation of local energy levels of metal ions within the band gap of the TiO_2 photocatalyst. Thus, the electronic properties of the TiO_2 become modified to a large extent and the photocatalyst shows clear response in the visible light region (Anpo and Takeuchi, 2003; Serpone et al., 1994). In fact, the preparation method plays an important role in the photocatalytic efficiency of prepared photocatalyst. Therefore, inserting different types of metal ions into TiO_2 lattice leads to different photocatalytic efficiencies. In some cases there is no photocatalytic activity noticed under visible light and lower activity even in the UV light region compared to non-doped photocatalysts. This retardation in the photocatalytic activity comes from high rate of recombination of charge carriers through the metal ion energy levels (Brezova et al., 1997; Fujishima and Zhang, 2006). Furthermore, doping of metal ions involves other drawbacks related to the thermal instability of the doped TiO_2, high-cost of ion-implantation facilities, and

fast electron trapping by the metal centers (Wang et al., 1999; Yamashita et al., 1998).

1.7.4 Doping of TiO_2 with non-metal atoms

Doping of TiO_2 lattice with non-metal atoms such as N (Kosowska et al., 2005), F (Mrowetz and Selli, 2006), S (Periyat et al., 2008), and C (Xiao et al., 2008) is considered as another widespread technological approach for enhancing the photocatalytic activity of TiO_2 by narrowing its band gap for larger absorption in the visible light region. For instance, narrowing band gap of N-doped TiO_2 can be achieved by substituting oxygen with nitrogen in the TiO_2 lattice. As a result, the corresponding N (2p) states are centered above the valence band edge. Hence, mixing of N (2p) states with O (2p) states leads to the reduction of the band gap of the N-doped TiO_2 and higher photocatalytic activity for the degradation of color and colorless pollutants can be achieved under visible light irradiation (Kosowska et al., 2005). Additionally, the photocatalytic activity of carbon-doped TiO_2 can be attributed to the presence of oxygen vacancy state between the valence band and conduction band due to the formation of Ti^{3+} in the system of carbon-doped TiO_2 (Xiao et al., 2008), or by narrowing the band gap or formed intra-gap localized level (Li et al., 2008). Even though excellent results can be achieved by applying this modification method, high consumption of energy is required due to the calcination process or heating treatment under specific conditions (Kosowska et al., 2005).

1.7.5 Utilizing different heterojunction systems

Heterojunction system means the coupling aspect of two different semiconductors such as CdS/TiO_2 and/or Bi_2S_3/TiO_2. Both heterojunction systems were prepared by two different methods, which are, either direct mixing of these semiconductors or by precipitation of one semiconductor which acts as sensitizer over the other semiconductor which acts as supported material. Thus, utilizing two semiconductors in contact with each other in different redox energy levels of their corresponding conduction bands and valence bands can improve separation process of electron-hole pair. This prolongs the life times of the charge carriers and as a result improves the efficiency of the interfacial charge to the adsorbed pollutants on the heterojunction system surface. However, the photocatalytic efficiency of the heterojunction system strongly depends on the preparation method, how good is the surface contact between the two semiconductors and the type of the treated substrate (Bessekhouad et al., 2004).

1.7.6 Utilization of thin films

Utilizing a fixed TiO_2 photocatalyst has very important operational advantages such as the time saved and photocatalyst material by eliminating the need of catalyst powder recovery during the photocatalytic process. However, the overall photocatalytic performance of the fixed TiO_2 thin films decrease compared to the corresponding slurry mode of the TiO_2 powder. Since the photocatalytic process is a surface phenomenon rather than volume or mass phenomenon (Damodar and Swaminathan, 2008), easy access to the light irradiation and organic pollutants is fundamental for the effective photocatalytic degradation. Thus, fixed TiO_2 thin film