

**SYNTHESIS, CHARACTERIZATION AND
ACTIVITY OF TITANIUM DIOXIDE BASED-
(Ca, Ce, W)-TiO₂ PHOTOCATALYSTS FOR
DEGRADATION OF DYE AND PESTICIDE**

by

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LIST OF SYMBOLS

Symbol	Description	Unit
A	constant	
A_S	Surface area	m^2/g
C, C_t	Concentration at any time, t	mg/L
C_0, C_{A0}	Initial concentration	mg/L
D_p	Crystallite size in nm of a characteristic peak	nm
e^-	Electron	
E_{bg}, E_g	band-gap energy	eV
E_{phot}	Photon Energy	eV
h^+	Hole	
$h\nu$	Photon energy	eV
H	Hysteresis type	
I_A, I_R	Intensities of strongest peaks of anatase (101) at $2\theta = 25.4^\circ$ and rutile (110) at $2\theta = 27.4^\circ$	
k'	Normalized rate constant	$g/(m^2 \cdot min)$
k, k_{app}	Apparent rate constant	(1/min)
k_r	True rate constant	mg/(L.min)
K	Dimensionless constant	
K_A	Adsorption equilibrium constant	L/mg
$\cdot OH$	Hydroxyl radical	
OH^-	Hydroxyl ion	
P	Pressure	bar

P_0	Initial pressure	bar
r_{A0}	Initial rate of reaction	mg/(L.min)
R	Reflectance for any intermediate energy Photon	%
R^2	Correlation coefficient	
R_{max} and R_{min}	maximum and minimum reflectance	%
t	Thin film thickness in reflectance spectra	nm
T_C	Calcination temperature	°C
V_P	Pore volume	cm ³ /g
$V_{\mu P}$	Micropore volume	cm ³ /g
W_R	rutile phase composition in the crystal	%
α	Attenuation constant	
$\beta_{1/2}$	Full-width at half maximum (FWHM)	radians
θ	Bragg's angle	degree.
θ_1, θ_2	Active sites (coverage)	
λ	Wavelength	nm

LIST OF ABBREVIATIONS

2,4-D	2,4-Dichlorophenoxy-acetic acid
AB25	Acid blue 25
ACs	Activated carbons
AOPs	Advanced oxidation processes
AR1	Acid red 1
BET	Brunauer–Emmet–Teller
BJH	Barret–Joyner–Halenda
CB	Conduction band
CdS	Cadmium sulphide
CO ₂	Carbon dioxide
DB71	Direct blue 71
DBS	dodecyl benzene sulphonate
EDCs	Endocrine-disrupting chemicals
EDX	energy dispersive X-ray
FTIR	Fourier transform infrared
HCl	Hydrochloric acid
H ₂ O	Water
H ₂ O ₂	hydrogen peroxide
I	Interaction
L-H	Langmuir-Hinshelwood
MB	Methylene blue
MO	Metal oxide
NBB	Naphthol Blue Black
NO	Nitrogen oxide

OG	Orange G
PHF	Polyhydroxy fullerenes
RB19	Reactive blue 19
RO16	Reactive orange 16
SDS	sodium dodecyl sulphonate
SEM, SSEM	surface scanning electron microscopy
SILAR	successive ionic layer adsorption and reaction
TEM	Transmission electron microscopy
TiO ₂	Titanium dioxide
TOC	Total organic carbon
UV	Ultra violet
VB	Valence band
wt%	Weight percent
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
ZnO	Zinc oxide
ZnS	Zinc sulphite

SINTESIS, PENCIRIAN DAN AKTIVITI FOTO PEMANGKINAN TITANIUM DIOKSIDA BERASASKAN (Ca, Ce, W) UNTUK DEGRADASI PEWARNA DAN RACUN PEROSAK.

ABSTRAK

Pengindustrian global berhadapan dengan berbagai cabaran. Pelepasan yang tidak diinginkan melibatkan produk dan bahan cemar yang karsinogen dan toksik ke dalam persekitaran oleh industri tekstil, kimia dan pemprosesan adalah berkadar langsung kepada pertumbuhan industri. Persekitaran harus dipastikan selamat. Maka, teknik fotopemangkinan telah dikaji untuk merawat air sisa yang mengandungi bahan pencelup (asid merah 1, reaktif oren 16, reaktif biru 19, terus biru 71 dan asid biru 25) dan racun serangga (asid 2-4-diklorofenoxiasetik; 2,4-D). Fotomangkin komposit yang stabil elektroniknya daripada jenis $Ti_{(1-x-y)}Ca_{(3x-y)}Ce_{(2x-y)}W_{(y/6)}O_{2(1-2(y-x))}$ (pada $y < 2x$ dan $x+y < 1$) dengan aktiviti fotopemangkinan yang lebih baik telah dibangunkan secara pencampuran TiO_2 dengan unsur Ca, Ce dan W. Fotopemangkinan ini telah disediakan dengan kaedah sol-gel, dirawat secara termal-hidro dan digunakan untuk menguraikan bahan-bahan tersebut di atas. Keberkesanan fotopemangkinan komposit disahkan dengan membandingkan aktiviti dengan dua fotopemangkinan komersial; Degussa P25 dan TiO_2 - Sigma pada keadaan ujikaji yang sama. Fotopemangkinan yang dibangunkan ini didapati lebih baik daripada Sigma - TiO_2 dalam penguraian AR1 secara fotopemangkinan solar. Ujian kebolegunaan ke atas fotopemangkinan yang dibangunkan ini membuktikan yang ia lebih baik berbanding Degussa P25 (yang mana tidak boleh mendak dari larutan selama tujuh bulan selepas degradasi fotopemangkinan ke atas 2,4-D). Ini membuktikan yang ia bukan boleh diguna semula. Sebaliknya, fotomangkin komposit dapat menguraikan pencemar kurang dari 1 jam selepas

pemancaran dan keberkesanannya pada kitaran keempat adalah masih sama seperti pada kitaran pertama. Kelebihan fotomangkin komposit ini ke atas Degussa P25 menghadkan bilangan perbandingan di antara mereka. Mangkin lain turut dibangunkan dan diuji. Fotomangkinan yang dibangunkan ini telah dicirikan oleh X-ray fotoelektron spektroskopi untuk unsur-unsur kimia, belauan sinar-X dan Fourier transformasi infra merah untuk pencirian struktur dan analisis kumpulan berfungsi; imbasan elektron mikroskop untuk mikrostruktur dan morfologi permukaan; jerapan nitrogen untuk penentuan luas permukaan dan taburan saiz liang; UV-Vis pantulan untuk penilaian 'band gap'. Keputusan pencampuran menghasilkan penurunan selajalur gelombang TiO_2 daripada 3.2 eV kepada 2.94 eV. Oleh itu, tidak balas fotopemangkinan beralih kepada kawasan tampak. Analisis XPS beresolusi tinggi menunjukkan fotomangkinan adalah lebih stabil kerana kehadiran kandungan kimia pada keadaan pengoksidaan yang dijangkan. Fotopemangkinan mempunyai luas permukaan yang besar dan jerapan-penyaherapan isoterma nitrogen jenis IV dengan kelok histerisis H2. Pelbagai parameter operasi seperti kepekatan awal bahan-bahan pencemar, pH awal, kalsinasi suhu/hidrotermal dan kandungan campuran telah dikaji. Walaupun pH mempengaruhi proses fotopemangkinan untuk semua keadaan, kepekatan awal di dapati tidak mempengaruhi proses kecuali bagi penguraian 2,4-D. Ujikaji kinetik mendapati tertib tindakbalas yang terbaik adalah tertib pertama, kecuali untuk penguraian cahaya yang boleh dilihat AR1 di mana kadar tidak bergantung kepada kepekatan awal.

SYNTHESIS, CHARACTERIZATION AND ACTIVITY OF TITANIUM DIOXIDE BASED-(Ca, Ce, W)-TiO₂ PHOTOCATALYSTS FOR DEGRADATION OF DYE AND PESTICIDE

ABSTRACT

Global industrialization is not without its attendant challenges. The release of unwanted by-products and pollutants which are carcinogenic and toxic into the environment by textiles, chemicals and processing industries is directly proportional to industrial growth. The environment must be kept safe. Therefore, photocatalysis leading to complete mineralization of pollutant(s) was adopted to treat wastewaters containing dyes (acid red 1, reactive orange 16, reactive blue 19, direct blue 71 and acid blue 25) and a pesticide (2,4-dichlorophenoxyacetic acid; 2,4-D). A composite photocatalyst, electronically stable of the type $Ti_{(1-x-y)}Ca_{(3x-y)}Ce_{(2x-y)}W_{(y/6)}O_{2(1-2(y-x))}$ (at $y < 2x$ and $x+y < 1$) with an enhanced photocatalytic activity was developed by doping TiO₂ with Ca, Ce and W. The photocatalyst was prepared by sol-gel method, hydrothermally treated and employed in the degradation of the above mentioned pollutants. The effectiveness of the composite photocatalyst was verified by comparing its activity under the same experimental conditions with two commercial photocatalysts; Degussa P25 and TiO₂-Sigma product CAS No. 1317-70-0. The developed photocatalyst was better than TiO₂-Sigma product in solar photocatalytic degradation of AR1. The reusability test of the developed photocatalyst makes it superior to Degussa P25 (which could not settle out of solution seven months after photocatalytic degradation of 2,4-D), hence rendering it non-reusable. On the other hand, the composite photocatalyst settled out of solution in less than 1 h after irradiation and proved to be as efficient at the fourth cycle as in the first, as it accomplished a complete degradation at the same irradiation time. This advantage of the composite photocatalyst over Degussa P25 limits the number of comparison

made between them. Other catalysts were also developed and tested as described in the body of the Thesis. The developed photocatalysts were characterized by X-ray photoelectron spectroscopy (XPS) for the chemical states of the elements in the developed photocatalysts; X-ray diffraction (XRD) and Fourier Transformed Infra Red (FTIR) for structural and functional groups analysis respectively; surface scanning electron microscopy (SEM) for microstructure and morphology; Nitrogen-physorption for surface area and pore size distributions; and UV-Vis diffused reflectance for band gap evaluations. The doping resulted in a reduction in the band gap of TiO_2 from 3.2 eV to 2.94 eV, and hence the photocatalytic reaction was pushed into the visible region. The high resolution XPS analysis revealed that the photocatalysts is stable as its chemical constituents were found to exist in the proposed oxidation states. The photocatalysts have high surface areas available for photocatalysis and are of N_2 adsorption-desorption isotherms of type IV with type H2 hysteresis loops. Various operational parameters such as initial pollutants concentration, initial pH, calcination/hydrotreatment temperatures and dopant contents were investigated. While pH greatly influenced the photocatalytic process in all cases, initial concentration does not seem to influence the process, except for 2,4-D degradation. The kinetic study revealed that reaction order that best describes the whole process is first order, except for the visible light degradation of AR1 where the rate is independent of initial concentration.

CHAPTER ONE

INTRODUCTION

The effluents, gaseous or liquid produced by some of our industries are harmful to the health and general well-being of man. When undesirable substances are present in liquid effluents, it can be disastrous as their presence pose severe threat to the immediate recipients. Wastewaters from various industries, factories, laboratories, etc are serious problems to the environment. The discharged wastes containing dyes are toxic to microorganisms, aquatic life and human beings (Borker & Salker, 2006). These deleterious effects of chemicals on the earth ecosystems are a cause for serious concern. Several of these chemicals such as azo dyes, herbicides, and pesticides are actually present in rivers and lakes, and are in part suspected of being endocrine-disrupting chemicals (EDCs) (Coleman *et al.*, 2000; Hong *et al.*, 1998; Ohko *et al.*, 2001; Wang and Hong, 2000).

Konstantinou and Albanis (2004) reported that textile dyes and other industrial dyestuffs constitute one of the largest groups of organic compounds that represent an increasing environmental danger. About 1-20 % of the total world production of dyes is lost during the dyeing process and is released in the textile effluents (Zollinger, 1991). The release of those coloured wastewaters in the environment is a considerable source of non-aesthetic pollution and eutrophication, and can originate dangerous byproducts through oxidation, hydrolysis, or other chemical reactions taking place in the wastewater phase. It must be noted that dyes can present toxic effects and reduce light penetration in contaminated waters (Prado, *et al.*, 2008).

Degradation of dyes in industrial wastewaters has therefore received increasing attention and some methods of remediation have been proffered. Most textile dyes are photocatalytically stable and refractory towards chemical oxidation (Arslan and Balcioglu, 2001), and these characteristics render them resistant towards decolorization by conventional biochemical and physico-chemical methods. Traditional physical techniques (adsorption on activated carbon, ultrafiltration, reverse osmosis, coagulation by chemical agents, ion exchange on synthetic adsorbent resins, etc.) have been used for the removal of dye pollutants (Tang and An, 1995; Konstantinou and Albanis, 2004). These methods only succeed in transferring organic compounds from water to another phase, thus creating secondary pollution. This will require a further treatment of solid-wastes and regeneration of the adsorbent which will add more cost to the process. Microbiological or enzymatic decomposition (Hao *et al.*, 2000), biodegradation (Sleiman *et al.*, 2007), ozonation (Slokar & Marechal, 1998), and advanced oxidation processes such as Fenton and photo-Fenton catalytic reactions (Kuo, 1992; Konstantinou and Albanis), H₂O₂/UV processes (Ince and Gonenc, 1997; Arslan *et al.*, 2001) have also been used for dyes removal from wastewaters.

Forgacs *et al.* (2004) noted that traditional wastewater treatment technologies have proven to be markedly ineffective for handling wastewater of synthetic textile dyes because of the chemical stability of these pollutants, and went further to verify that 11 out of 18 azo dyes selected for their investigations passed through the activated sludge process practically untreated. All the aforementioned processes have a wide range of their deficiencies in the removal of dyes from wastewaters.

Recent studies (Stylidi *et al.*, 2003; Silva *et al.*, 2006; Sun *et al.*, 2006; Reddy *et al.*, 2007; Sleiman *et al.*, 2007; Saquiba *et al.*, 2008; Li *et al.*, 2009; Kansal *et al.*, 2010; Zhang *et al.*, 2011) have been devoted to the use of photocatalysis in the removal of dyes from wastewaters, particularly, because of the ability of this method to completely mineralize the target pollutants (Madhavan, *et al.*, 2008).

Among the AOPs, heterogeneous photocatalysis using TiO₂ as a photocatalyst appears as the most emerging destructive technology (Hoffmann, 1995; Su *et al.*, 2004; Sun *et al.*, 2006; Saquiba *et al.*, 2008; Zhang *et al.*, 2011). The key advantage of the former is its inherent destructive nature. Photocatalysis can be carried out under ambient conditions (atmospheric oxygen is used as oxidant), and may lead to complete mineralization of organic carbon into CO₂ without any mass transfer operation. TiO₂ choice as a photocatalyst is made because it is largely available, inexpensive, and non-toxic and relatively stable-chemically. Moreover, works have been reported on the photocatalytic potentials of TiO₂ (Zhang and Liu, 2008). Titanium dioxide (TiO₂) has been very effective photocatalyst, but its effectiveness is impaired by its high band gap energy. These therefore, demand modifications for the effective application of TiO₂ as a photocatalyst. Hence in order to enhance interfacial charge-transfer reactions, the catalyst has been modified by selective ion doping of the crystalline TiO₂ matrix (Chen *et al.*, 2007; Huang *et al.*, 2008; Kryukova *et al.*, 2007; Ozcan *et al.*, 2007; Rengaraj *et al.*, 2006; Sun *et al.*, 2006; Wei *et al.*, 2007; Zhiyong *et al.*, 2007, 2008).

Various metal ions – rare earth (Xu *et al.*, 2002; Saif and Abdel-Mottaleb, 2007; Wei *et al.*, 2007), transition (Wilke and Breuer, 1999; Jeon *et al.*, 2000; Li *et al.*, 2001; Xu *et al.*, 2004; Liu *et al.*, 2005; Stir *et al.*, 2006; Ghorai *et al.*, 2007; Liao

et al., 2007; Xin *et al.*, 2008; Zhang and Lei 2008; Huang *et al.*, 2008; Ding *et al.*, 2008; Fan *et al.*, 2008; Cheng 2011), other metal ions (Sun *et al.*, 2006; Rengaraj and Li, 2006; Rengaraj *et al.*, 2006), co-doping (Ghorai *et al.*, 2007; Srinivasan *et al.*, 2006; Colmenares *et al.*, 2006; Bettinelli *et al.*, 2007; Shi *et al.*, 2007; Gu *et al.*, 2008; Liu *et al.*, 2008; Zhang and Liu, 2008), non-metal ions (Ohno *et al.*, 2004; Liu *et al.*, 2006; Sun *et al.*, 2007; Yu *et al.*, 2007; Peng *et al.*, 2008; Li *et al.*, 2008; Zaleska *et al.*, 2008; Li *et al.*, 2008; Zhang *et al.*, 2008b; Crisan *et al.*, 2008) and surfactants (Liao *et al.*, 2007) have been used to enhance the photocatalytic activities of TiO₂. It must be noted that though transition metals ions such as Cr, V, Fe, etc, have been used in doping TiO₂ photocatalyst, doping with transition metal ions generally increase carrier-recombination centers, and consequently debases the quantum efficiency of doped TiO₂ catalysts (Gu *et al.*, 2008). Moreover, doping with transition metal ions could result in thermal instability of the doped photocatalysts (Gu *et al.*, 2008). Anpo (2000) reported on doping TiO₂ with transition metals and their effects on the photocatalytic decomposition of NO. Two doping conditions were considered in his study; (i) the metal ions implanted TiO₂ and (ii) doping TiO₂ with the considered metal chemically. In both methods it was discovered that the doping had negative influence on the photocatalytic efficiency of TiO₂ even under UV light irradiation ($\lambda < 380\text{nm}$), that is to say that the photocatalytic efficiency of TiO₂ decreased with the doping. It was however noted that for the photocatalytic decomposition of NO, only Cr and V ion-implanted TiO₂ retained the same photocatalytic efficiency as the original unimplanted TiO₂ even under UV light irradiation ($\lambda < 380\text{nm}$). This further explains why transition metal doping should be considered with utmost care.

There have been many reports on transition metal, rare earth and noble metal

ions doping of TiO₂, but studies on alkaline-earth metal ions doping of TiO₂ and their photocatalytic properties have limited literature. The only literature available at the time of preparing this report is that reported by Li *et al.*, (2007). The Researchers reported on the effect of doping TiO₂ with alkaline-earth metal ions and its photocatalytic activity on the photocatalytic generation of hydrogen in suspension. No report has been seen on doping TiO₂ with alkaline earth metal ions for photocatalytic degradation of textile wastewater. This has therefore been the driving force of this work. This present work was therefore aimed at developing doped and undoped photocatalysts for the photocatalytic degradation of textile dyes in textile wastewaters, with priority to TiO₂ doped with alkaline earth and other metals ions.

1.1 Problem Statement

It is certain that a good society needs a good health condition and for this to take place, the environment, in totality must be kept free from threat of any kind. It is also a known fact that industrial effluents are in part major cause of environmental pollution. Most of the industries like textile, leather, plastics, paper, food, cosmetic and many others use dyes and pigments to colour their products, and the coloured wastewaters are always released into the water channels. These coloured wastewaters from these industries are harmful to aquatic life in rivers and lakes, due to reduced light penetration and the presence of highly toxic metal complex dyes. The release of these coloured wastewaters into the environment is a considerable source of non-aesthetic pollution and eutrophication and can originate dangerous by-products through oxidation, hydrolysis, or other chemical reactions taking place in the wastewater phase. Noting also that about 70% of the industries in Malaysia

falls into the group of industries described above; the wastewaters from these industries must then be purified before release into water channels.

In purifying wastewaters some traditional physical techniques (adsorption on activated carbon, ultra-filtration, reverse osmosis, coagulation by chemical agents, ion exchange on synthetic adsorbent resins, etc.) have been used for the removal of dye pollutants. These methods only succeed in transferring organic compounds from water to another phase, thus creating secondary pollution. Other methods such as chlorination and ozonation have also been used, but the rates of removal are slower, and have high operating costs and limited effect on carbon content. It is on this background that many Researchers have developed advanced oxidation techniques for the degradation of dyes in wastewaters. Among the advanced oxidation techniques, is photocatalysis using TiO_2 and this has been found to be very efficient, but has a limit due to the high electrons-holes recombination that exists in this photocatalyst. In view of this, the present study is set out to develop doped and undoped photocatalysts for the photocatalytic degradation of chemical pollutants. As already been mentioned, chemical pollutants, such as dyes and pesticides are sources of environmental pollutions when they are released into the environment and they are majorly released into the water channels by Chemical industries. These pollutants must be removed from wastewater before discharge into the water channels. This research was therefore designed to treat wastewaters containing dyes and pesticides through titanium dioxide-based photocatalysis which possess the potentials of total mineralization of the targeted pollutant. The outcome of this research will chart a pathway for the purification of wastewaters from industries, which will be very helpful in keeping the environment free from these harmful chemicals.

1.2 Research Objectives

The present Research study was aimed at developing a reusable doped photocatalysts for the photocatalytic degradation of textile dyes and pesticide (2,4-dichlorophenoxyacetic acid). This aim was achieved via the following objectives:

To

- i. Develop doped and undoped photocatalysts using Titanium butoxide as precursor photocatalyst.
- ii. Study the activity and effectiveness of the developed doped and undoped photocatalysts by using them to degrade dyes and pesticide.
- iii. Study both the kinetic and process parameters effects on the activities of the developed photocatalysts under UV, solar and visible lights irradiation on the photocatalytic degradation of dyes and pesticide.
- iv. Study the physical and chemical characteristics of the developed doped and undoped photocatalysts.

1.3 Scope of study

The scope of the present study covered the development, optimization and comparative studies of titanium dioxide (TiO_2) based photocatalysts, and test of their photocatalytic efficiency with the degradation of textile dyes and a pesticide (2,4-dichlorophenoxyacetic acid; 2,4-D). It also involved characterization of the developed photocatalysts using XPS for the chemical states of the elements in the developed photocatalysts; X-ray diffraction (XRD) and Fourier Transformed Infra Red (FTIR) for structural and functional groups analysis respectively; surface scanning electron microscopy (SEM) for microstructure and morphology; Nitrogen-

physisorption for surface area and pore size distributions; and UV-Vis diffused reflectance for band gap evaluations. The scope also extended to the evaluation of the effects of operational parameters in photocatalytic degradation experiments.

1.4 Organization of the thesis

This thesis consists of five chapters. Chapter one (Introduction) presents the environmental problems associated with the release of industrial wastewater into the environment. It also enumerates the existing methods for the treatment of industrial wastewaters and points out the merits of photocatalysis over other methods. This chapter presents the problem statement, the objective of the research, scope and justification for embarking upon the research.

Chapter two (Literature Review) divulges information on the past studies in the area of the present studies and provides a routing for the photocatalysts development. It presents the merits and demerits of TiO_2 and proposed possible means of enhancement of the photocatalyst's (TiO_2) activity. The influences of operational parameters on the photocatalytic degradation of pollutants are discussed.

Chapter three (Materials and Methods) explains in details the materials, chemicals used and the research methodology employed in the present study. Detailed experimental setup including a step-wise description of the photocatalysts development, process conditions and photocatalysts characterizations are outlined in this chapter.

Chapter four (Results and Discussion) is the main thrust of the thesis which discusses, interprets and analyzes the results obtained in the present investigations.

The chapter is divided into eight major sections; which are development of photocatalyst for photocatalytic processes, characterization of photocatalysts, photocatalytic degradation of AR1 dyes by calcined TiO₂-based photocatalysts under UV light irradiation, photocatalytic degradation of reactive orange 16 (RO16) dyes by the 0.5 wt% Ca-TiO₂, degradation of dyes by hydrotreated photocatalysts, photocatalytic degradation of AR1 under visible light, degradation of 2,4-dichlorophenoxyacetic acid, and kinetic model.

Chapter five (Conclusions and recommendations) recapitulates the results reported in this study and presents recommendations for future studies in the field.

CHAPTER TWO

SURVEY OF LITERATURE

This chapter provides information on previous investigations in the current area of interest (photocatalysis). It explains the concept of photocatalysis; discusses on the types of semiconductor photocatalysts and charted a path for choosing TiO₂ as the semiconductor photocatalyst-base in the current studies. It also present information on different methods used in the preparation of TiO₂-baesd photocatalysts and also presents justification for the decision to employ sol-gel method in the preparations of the photocatalysts in the present investigations. Effects of operational parameters and other related topics are also considered.

2.1 Photocatalysis

Photocatalysis may be termed as a photoinduced reaction which is accelerated by the presence of a catalyst (Mills and Hunte, 1997). These types of reactions are activated by absorption of a photon with sufficient energy (equals or higher than the band-gap energy (E_{bg}) of the catalyst) (Carp *et al.*, 2004). The absorption leads to a charge separation due to promotion of an electron (e^-) from the valence band of the semi-conductor catalyst to the conduction band (CB), thus generating a hole (h^+) in the valence band (the schematic diagram of the process is presented in Figure 2.1).

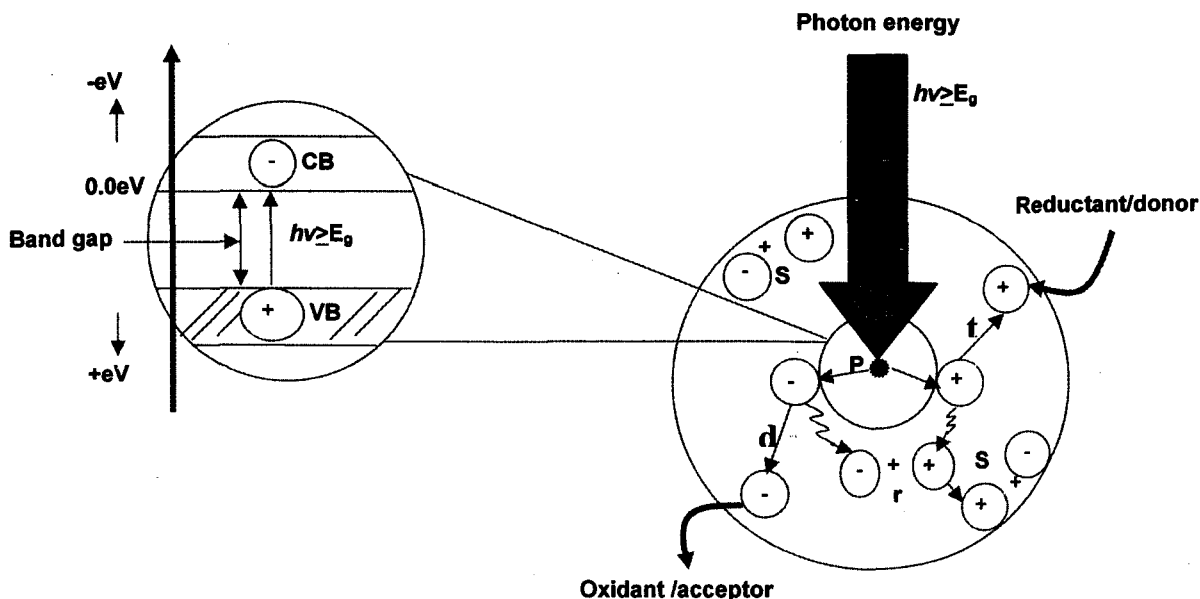
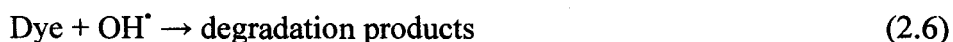
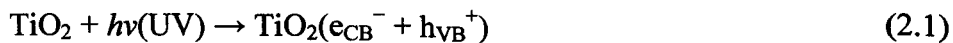


Figure 2.1. Schematic diagram of photocatalytic process initiated by photon acting on the semiconductor

Legend: p-photogenerated electron/hole pair, s-surface recombination, r-recombination in the bulk, d-diffusion of acceptor and reduction on the surface of semiconductor (SC), t-oxidation of donor on the surface of SC particles

The recombination of the electron and the hole must be prevented as much as possible if a photocatalyzed reaction must be favoured. The ultimate goal of the process is to have a reaction between the activated electrons with an oxidant to produce a reduced product, and also a reaction between the generated-holes with a reductant to produce an oxidized product. The photogenerated electrons could reduce the dye or react with electron acceptors such as O_2 adsorbed on the Ti(III)-surface or dissolved in water, reducing it to superoxide radical anion $O_2^{\cdot-}$ (Konstantinou and Albanis, 2004). The photo-generated holes can oxidize the organic molecule to form R^+ , or react with OH^- or H_2O oxidizing them into $\cdot OH$ radicals. Together with other highly oxidant species (peroxide radicals) they are reported to be responsible for the heterogeneous TiO_2 photodecomposition of organic substrates as dyes. According to this, the relevant reactions at the

semiconductor surface causing the degradation of dyes can be expressed as follows:



where $h\nu$ is photon energy required to excite the semiconductor electron from the valence band (ν_{VB}) region to conduction band (CB) region. The resulting OH^\bullet radical, being a very strong oxidizing agent (standard redox potential +2.8 V) can oxidize most of azo dyes to the mineral end-products.

2.2 Semiconductors

Semiconductors (such as TiO_2 , ZnO , Fe_2O_3 , CdS , and ZnS) can act as sensitizers for light-induced redox-processes due to the electronic structure of the metal atoms in chemical combination, which is characterized by a filled valence band, and an empty conduction band (Hoffmann *et al.*, 1995). Upon irradiation, valence band electrons are promoted to the conduction band leaving a hole behind. These electron-hole pairs can either recombine or can interact separately with other molecules. The holes may react either with electron donors in the solution, or with hydroxide ions to produce powerful oxidizing species like hydroxyl (oxidation potential 2.8 V) or super oxide radicals (Tang and An, 1995b).

In other word, semiconductor materials are materials whose valence band and conduction band are separated by an energy gap or band-gap. When a semiconductor molecule absorbs photons with energy equal or greater than its band-gap, electrons in the valence band can be excited and jump up into the conduction band, and thus charge carriers are generated. In order to have a photocatalyzed reaction, the e^-h^+ recombination, subsequent to the initial charge separation, must be prevented as much as possible (Gerven *et al.*, 2007).

Among all these semiconductors, the most widely used semiconductor catalyst in photoinduced processes is titanium dioxide (TiO_2). Though TiO_2 has the disadvantage of not being activated by visible light, but by ultraviolet (UV) light, it is advantageous over the others in that it is chemically and biologically inert, photocatalytically stable, relatively easy to produce and to use, able to efficiently catalyze reactions, cheap and without risks to environment or humans (Carp *et al.*, 2004).

2.2.1 Titanium dioxide photocatalyst

Titanium dioxide (TiO_2) or titania is a very well-known and well-researched material due to the stability of its chemical structure, biocompatibility, physical, optical and electrical properties. It exists in four mineral forms (Gianluca *et al.*, 2008), viz: anatase, rutile, brookite and titanium dioxide (B) or TiO_2 (B). Anatase type TiO_2 has a crystalline structure that corresponds to the tetragonal system (with dipyramidal habit) and is used mainly as a photocatalyst under UV irradiation. Rutile type TiO_2 also has a tetragonal crystal structure (with prismatic habit). This

type of titania is mainly used as white pigment in paint. Brookite type TiO_2 has an orthorhombic crystalline structure. TiO_2 (B) is a monoclinic mineral and is a relatively newcomer to the titania family. TiO_2 , therefore is a versatile material that finds applications in various products such as paint pigments, sunscreen lotions, electrochemical electrodes, capacitors, solar cells and even as a food coloring agent (Meacock, *et al.*, 1997) in toothpastes.

The possible application for this material as a photocatalyst in a commercial scale water treatment facility is due to several factors:

- (a) Photocatalytic reaction takes place at room temperature.
- (b) Photocatalytic reactions do not suffer the drawbacks of photolysis reactions in terms of the production of intermediate products because organic pollutants are usually completely mineralized to non-toxic substances such as CO_2 , HCl and water (Guillard, *et al.*, 2003; Aramendia *et al.*, 2005; Pichat, 2003; Malato *et al.*, 2003).
- (c) The photocatalyst is inexpensive and can be supported on various substrates such as, glass, fibers, stainless steel, inorganic materials, sand, activated carbons (ACs); allowing continuous re-use.
- (d) Photogenerated holes are extremely oxidizing and photogenerated electrons reduce sufficiently to produce superoxides from dioxygens (Fujishima, *et al.*, 2000).

Upon all the good qualities of titanium dioxide, it suffers the disadvantage of not being activated by visible light, but by ultraviolet (UV) light because of its high band gap energy. It also has a high rate of electrons-holes recombination, and this always impaired its effectiveness, and limits its range of operations. Nevertheless, the effectiveness of TiO_2 photocatalyst can be enhanced by doping metal and non-metal ions into it. The following investigations are the proofs of enhancement of the

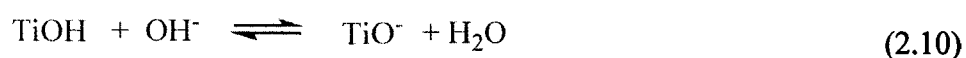
efficiency of TiO₂ by doping (Sun *et al.*, 2006; Sun *et al.*, 2008; Zhiyong *et al.*, 2007, 2008; Huang *et al.*, 2008; Wei *et al.*, 2007; Chen *et al.*, 2007; Rengaraj *et al.*, 2006; Yu *et al.*, 2007; Kryukova *et al.*, 2007; Ozcan *et al.*, 2007). Krishna *et al.* (2008) also reported a 2.6 times higher rate coefficient for PHF-TiO₂ over TiO₂ for the degradation of triazine monoazo compound Pricion red MX-5B.

2.3 Operating Parameters in Photocatalytic Processes

In photocatalytic degradation of dyes in wastewaters, the followings are operating parameters which affect the process: pH of the solution to be degraded, and the pH of the precursor solution (catalyst's solution during preparation of catalyst); oxidizing agent, calcination temperature, dopant content, and catalyst loading. These parameters will be considered one after the other as they influenced the photocatalytic processes of the degradation of dyes in wastewaters.

2.3.1 Influence of pH on photocatalytic degradation of dyes in wastewaters

The interpretation of pH effects on the efficiency of dye photodegradation process is a very difficult task because of its multiple roles (Konstantinou, and Albanis, 2004). First, is related to the ionization state of the surface according to the following reactions:



as well as to that of reactant dyes and products such as acids and amines. pH changes can thus influence the adsorption of dye molecules onto the TiO₂ surfaces,

an important step for the photocatalytic oxidation to take place (Fox and Dulay, 1993). Bahnemann *et al.* (1995) have already reviewed that acid-base properties of the metal oxide surfaces can have considerable implications upon their photocatalytic activity.

Second, hydroxyl radicals can be formed by the reaction between hydroxide ions and positive holes. The positive holes are considered as the major oxidation species at low pH, whereas hydroxyl radicals are considered as the predominant species at neutral or high pH levels (Tunesi and Anderson, 1991). It was stated that in alkaline solution, $\cdot\text{OH}$ are easier to be generated by oxidizing more hydroxide ions available on TiO_2 surface, thus the efficiency of the process is logically enhanced (Concalves *et al.*, 1999). Similar results are reported in the photocatalyzed degradation of acidic azo dyes and triazine containing azo dyes (Tang and An, 1995a; Reutergarth and Iangpashuk, 1997; Guillard *et al.*, 2003), although it should be noted that in alkaline solution there is a Coulombic repulsion between the negative charged surface of photocatalyst and the hydroxide anions. This fact could prevent the formation of $\cdot\text{OH}$ and thus decrease the photooxidation.

Third, it must also be noted that TiO_2 particles tend to agglomerate under acidic condition and the surface area available for dye adsorption and photon absorption would be reduced (Fox and Dulay, 1993). The degradation rate of some azo dyes increased with decrease in pH as reported elsewhere (Sakthivel *et al.*, 2003).

The study of Baran *et al.*, (2008) also showed that the degradation of Bromocresol purple dye under acidic condition was better than in alkaline medium, and that the molecules are positively charged. Precisely, after the solution was

acidified from pH 8.0 to pH 4.5, a 6-fold increase in adsorption efficacy was observed. Such an increase in adsorption efficacy could not be explained only through changes of the TiO₂ surface (probably caused by a change of pH (Wang *et al.*, 2000)).

The mechanism of the photocatalytic reaction in the presence of TiO₂ consists of a free radical reaction initiated by UV light (Baran *et al.*, 2008). The mechanism may depend on the ability of the degraded compound to be adsorbed on the surface of the catalyst. The extent of such adsorption depends on many factors, such as the charge of the degraded compound. It was found that in photocatalytic degradation, the adsorption level on unmodified TiO₂ is higher for dyes with a positive charge (cationic) than for those with a negative charge (anionic) (Baran *et al.*, 2003). As the charge depends on the pH of a given solution, it follows that both pH and the nature of a particular dye influence the photocatalyst activity (Grosse and Lewis, 1998; Poulios and Aetopoulou, 1999; Poulios *et al.*, 2000; Tang and An, 1995a,b; Alaton and Balcioglu, 2001).

The degradation rate of azo dyes increases with decrease in pH (Konstantinou and Albanis). At pH<6, a strong adsorption of the dye on the TiO₂ particles is observed as a result of the electrostatic attraction of the positively charged TiO₂ with the dye. At pH>6.8 as dye molecules are negatively charged in alkaline media, their adsorption is also expected to be affected by an increase in the density of TiO⁻ groups on the semiconductor surface. Thus, due to Coulombic repulsion the dyes are scarcely adsorbed (Abo-Farha, 2010; Lachheb *et al.*, 2002).

The effects of pH on photocatalytic degradation of dyes have been studied by many Researchers (Borker & Salker, 2006; Rengaraj *et al.*, 2006; Sun *et al.*, 2006;

Wei *et al.*, 2007; Chen *et al.*, 2007; Sun *et al.*, 2008; Xiao *et al.*, 2007; Baran *et al.*, 2008; Huang *et al.*, 2008; Saquib *et al.*, 2008; Yap *et al.*, 2010). Chakrabarti and Dutta (2004) studied the effects of pH in the photocatalytic degradation of two model dyes: methylene Blue and Eosin Y in wastewater using ZnO as the semiconductor catalyst. With two things in mind; one, industrial effluents may not be neutral, and two, pH of the reaction mixture influences the surface-charge-properties of the photocatalysts, they went on to investigate the effect of pH on the rate of degradation of dye at the pH range of 5.5-9.7, using 50 mg/L methylene Blue solutions. Their results revealed that the percentage degradation of the dye increased from 49 to 62 in 2 h as the pH increased from 5.5 to 9.7. This shows that change in pH shifts the redox-potentials of the valence and conduction bands, which may affect interfacial charge-transfer.

Borker and Salker (2006) in their work - photocatalytic degradation of textile azo dye over $Ce_{1-x}Sn_xO_2$ series reported on the effect of pH on the photocatalytic degradation of diazo dye Naphthol Blue Black (NBB). Their findings showed that degradation of the dye was faster in alkaline medium pH. It has earlier been reported that in alkaline medium, there is a greater probability for the formation of hydroxyl radical ($\cdot OH$), which can act as an oxidant, thus increasing the rate of photodegradation of the dye (Zhang, 2002).

Sleiman *et al.* (2007) reported on the influence of pH on the photocatalytic degradation of Metanil Yellow, an anionic dye with a sulfonate group, over TiO_2 photocatalyst under UV illumination. Their results indicated that the process efficiency is not considerably affected over a wide range of pH (4-8). They added that the interpretation of pH effect can be principally explained by a modification of

the electrical double layer of the solid-electrolyte interface, which consequently affects the sorption-desorption processes and the separation of the photogenerated electron-hole pairs at the surface of the semiconductor particles. Their study also explained that since Metanil Yellow is an anionic dye and has a sulfonate group, its adsorption is favoured at low pH (the extent of adsorption is almost twofold at pH 4.0 compared to that at neutral pH). The results of their findings showed that the nature of the substance to be degraded affects the operating pH of the system.

Zhiyong *et al.* (2007) in their work - ZnSO₄-TiO₂ doped catalyst with higher activity in photocatalytic processes, reported on the effect of pH on the photocatalytic degradation of Orange II, an anionic dye with -SO₃ group. Their results showed that the photocatalytic activity was most favoured at a lower pH (3.0), but went on at a slower and inefficient rate at pH 10.0. It is important to note that the photocatalytic degradation of some dyes are more effective at about neutral pH (Chen *et al.*, 2007), and others in alkaline medium (Saqiba *et al.*, 2008). It has earlier been reported that in alkaline medium, there is a greater probability for the formation of hydroxyl radical ([•]OH), which can act as an oxidant, thus increasing the rate of photodegradation of the dye (Zhang *et al.*, 2002).

In summary, Table 2.1 presents pH influence on the photodegradation of various dyes and an insecticide. The table reveals that different dyes have different activity in photocatalytic reaction. Some are photocatalytically degraded at lower pH, while others do so at higher pH. All these may be attributed to the nature of the pollutant to be degraded. Therefore, it is important to study the nature of the pollutants to be degraded, and determine the probably right pH to photocatalytically degrade them.

Table 2.1. pH influence on the photocatalytic degradation of various dyes and an insecticide

Pollutant type	Light source	Photocatalyst	Tested pH range	Optimum pH	References
Bisphenol-A	Solar	TiO ₂ /AC	3.0-11.0	3.0	Yap <i>et al.</i> , (2010)
Direct Blue DB53	UVC	Gd-TiO ₂	2.0-9.0	4.0	El-Bahy <i>et al.</i> , (2009)
Acid Orange 7	Visible	WO _x /TiO ₂	1.0-9.0	3.0	Sajjad <i>et al.</i> , (2010)
Methyl Orange	Visible UV	WO _x /TiO ₂ Pt-TiO ₂	1.0-9.0 2.5-11.0	4.0 2.5	Sajjad <i>et al.</i> , 2010 Huang <i>et al.</i> (2008)
Orange Green	UV Visible	Sn/TiO ₂ /AC N-TiO ₂	1.0-12.0 1.5-6.5	2.0 2.0	Sun <i>et al.</i> (2008) Sun <i>et al.</i> (2008)
Fast Green	UV	TiO ₂	3.0-11.0	4.4	Saquiba <i>et al.</i> (2008)
Patent Blue VF	UV	TiO ₂	3.0-11.0	11.0	Saquiba <i>et al.</i> (2008)
Everdirect Blue (BRL)	UV	K-TiO ₂	4.5-11.8	7.2	Chen <i>et al.</i> (2007)
Orange II	Solar	Zn-TiO ₂	3.0-10.0	3.0	Zhiyong <i>et al.</i> (2007)
Acid Red B	UV	Ce-TiO ₂	1.5-7.0	1.5	Wei <i>et al.</i> (2007)
Bromocresol Purple	UV	TiO ₂	4.5 and 8.0	4.5	Baran <i>et al.</i> (2008)
4-Chlorophenol	UV	N-TiO ₂	2.0-5.0	3.0 ^a	Yu <i>et al.</i> (2007)
Salicylic Acid	UV	TiO ₂	1.0-11.0	2.3 ^a	Su <i>et al.</i> (2004)

^a pH of precursor solution (catalysts solution during preparation of catalysts).

Influence of pH of the solution of precursor on the photocatalytic activity had also been studied (Yu et al, 2007). In this case, photocatalysts were prepared at different pH range (2.0-5.0), and calcined at the same temperature, 500°C. The photocatalytic activity of N-doped TiO₂ nanoparticles was found to increase as the pH decreased from 5.0 to 3.0. Further decrease in pH to 2.0 affected the photocatalytic activity of the catalyst negatively. Hence, the optimum pH for that particular catalysts' preparation was 3.0. The reason advanced for the adverse effect of low pH on the photocatalyst performance is that the possible increase of H⁺ concentration may restrain hydrolyzation of Ti(OBu)₄ and thereby reduce the crystal size of the prepared N-doped TiO₂ nanoparticles. Again, too low pH such as 2.0 would result in phase transformation from anatase to rutile (Chen and Gu, 2002).

2.3.2 Oxidizing agents effect on photocatalytic degradation of dyes in wastewaters

Reports show that oxidizing agents have a great deal of influence on the photocatalytic degradation of dyes. It was demonstrated by Saquib *et al.* (2008) that hydrogen peroxide (H₂O₂), ammonium persulphate ((NH₄)₂S₂O₈) and potassium bromate (KBrO₃) have individual influence on the degradation of Fast Green FCF (1) and Patent Blue VF (2) using Hombikat UV 100 and Degussa P25 as respective photocatalysts. Their results revealed that potassium bromate and ammonium persulphate had a beneficial effect on the degradation rate for the decomposition of dye 1 in the presence of UV 100; whereas in the case of dye 2, all the electron acceptors were found to enhance the rate markedly in the presence of P25.

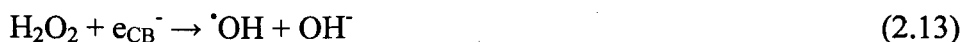
Huang *et al.* (2008) also studied the effect of adding H₂O₂ on the decolorization of methyl orange. The decolorization rate was found to increase with

increase in H_2O_2 concentration. The experiment was conducted at the concentration range of 0.4 to 2 mM/L H_2O_2 . They reported an optimum addition of 1.2 mM/L H_2O_2 for photocatalytic discolorization of methyl orange solution by Pt modified TiO_2 loaded on natural zeolite. Actually, addition of H_2O_2 enhanced the reaction. Zhiyong *et al.* (2008) also reported that addition of H_2O_2 (1 mM) to methyl orange solution mediated TiO_2 Degussa P25 (0.5 g/L) under sunlight irradiated photocatalyst brought about methyl orange degradation in 1 h.

Oxygen is required as electrons scavenger to keep the photocatalytic reaction, and the amount of oxygen going into the system is an important parameter. The air (oxygen) flow into the photocatalytic system should be well regulated, as poor flow of oxygen can bring about an adverse effect on the photocatalytic reaction as reported by Chakrabarti and Dutta, (2004). Chakrabarti and Dutta (2004), in their work-Photocatalytic degradation of model textile dyes in wastewater using ZnO as semiconductor catalyst, studied the effect of air flow into the reaction medium for the PCD of Eosin Y. The airflow rate was in the range from 0 to 11.3 L/min. The results showed an increasing effect throughout the range under study. Nevertheless, when there was no airflow, the reaction seemed to be better favoured than at 6.13 L/min airflow rate for the first 90 min, but ended up at the same point at 120 min reaction time. This is an indication that poor airflow can adversely affect the photocatalytic reaction.

Konstantinou and Albanis (2004) affirmed that H_2O_2 and $\text{S}_2\text{O}_8^{2-}$ were beneficial for the photooxidation of the dyes of different chemical groups including azo dyes. This is in conformity with the findings of Augugliaro *et al.* (2002) and, Saquib and Muneer (2003). The reactive radical intermediates (SO_4^- and $\cdot\text{OH}$)

formed from these oxidants by reactions with the photogenerated electrons can exert a dual function: as strong oxidant themselves and as electron scavengers, thus inhibiting the electron-hole recombination at the semiconductor surface (Sun *et al.*, 2006) according to the following equations:



It must be noted that the addition of peroxide increases the rate towards real reaction with adequate oxygen supply, because the solution phase may at times be oxygen starved as a result of either oxygen consumption or slow oxygen mass transfer. The presence of persulphate positively affects the mineralization rate, despite the decrease of pH as the oxidant properties of the system probably prevail on the effect of pH reduction.

Other works (Sun *et al.*, 2006; 2008; Yang *et al.*, 2010; Puangpetch *et al.*, 2011) have also revealed the effect of oxidants in photocatalytic reactions. It was pointed out as part of their findings that one practical problem in using TiO_2 as photocatalysts is the undesired electron-hole recombination, which in the absence of proper electron acceptor or donor, is extremely inefficient and thus represents the major energy-wasting step, thereby limiting the achievable quantum yield. They therefore opined that, one strategy to inhibit electron-hole recombination is to add irreversible electron acceptors to the reaction system, and they used H_2O_2 to study its effect on photodegradation of Orange G (OG) on the N-doped TiO_2 under

different light sources. The results indicated that there was an optimal dosage of H_2O_2 , at which the degradation efficiency of OG on the N-doped TiO_2 attained the height. At higher dosage of H_2O_2 beyond the optimum, the degradation efficiency of OG decreased. This was because the very reactive $\cdot\text{OH}$ radicals and valence band holes could be consumed by H_2O_2 itself as given in equations (2.16-2.18) (Mahmoodi, *et al.*, 2006; Coleman *et al.*, 2007). At the same time, radical-radical recombination as a competitive reaction must be taken into account, as described in Eq. (2.19) (Konstantinou and Albanis, 2004).



As both OH and h_{VB}^+ are strong oxidants for organic pollutants, the photocatalytic degradation of OG will be inhibited in the condition of excess of H_2O_2 . Furthermore, H_2O_2 can be adsorbed onto TiO_2 particles to modify their surfaces and subsequently decrease its catalytic activity (Tanaka *et al.*, 1989).

Again, the wavelength and intensity of the light sources affect the H_2O_2 performance as oxidizing agent in photocatalytic degradation of organic pollutants. This was also demonstrated by Sun *et al.* (2006). Their findings revealed that the optimal dosage of H_2O_2 for photodegradation of OG under sunlight was 5.0 mM/L, while under visible light was 15.0 mM/L.

In order to improve on the performance of photocatalytic reaction of Bi^{3+} doped TiO_2 , Rengaraj and Li (2007), used formic acid with a simple one-carbon