

**SYNTHESIS OF IMMOBILIZED NANO-TiO₂ FOR
PHOTOCATALYTIC DEGRADATION OF
PHENOL**

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DEGRADATION OF PHENOL**

by

NOR FAUZIAH BINTI ZAINUDIN

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LIST OF SYMBOLS

Symbol	Description	Unit
A	Anatase	-
C	Phenol concentration	mg/L
C _o	Initial phenol concentration	mg/L
dC/dt	Differential of C polynomial with respect to t	mg/L.min
E_r	Relative error	-
\bar{E}	Mean % of relative error	-
k	Reaction rate constant	mg/L.min
K	Adsorption equilibrium constant	L/mg
k_{app}	apparent rate constant	min ⁻¹
R	Rutile	-
R ²	Correlation coefficient	-
T	Temperature	°C
(-r)	Reaction rate	mg/Lmin
(-r) _o	Initial rate of reaction for phenol degradation	mg/L.min
t	Time	min
V	Volume of treated phenol solution	L
W _{TiO2}	Weight of TiO ₂ film	g
W _A	Mass fraction of anatase	-
W _R	Mass fraction of rutile	-
w/w	Ratio of weight over weight	-
x ₁	Coded term of initial phenol concentration	mg/L

x_2	Coded term of initial pH	-
x_3	Coded term of H ₂ O ₂ concentration	mg/L

Greek Symbols

θ	Angle between the incidence ray and reflection to the plane (degree)
α	Distance of the axial runs from the design center
λ	Wavelength of the UV lamp (nm)

LIST OF ABBREVIATIONS

AOP	Advanced oxidation processes
BET	Brunauer-Emmett-Teller
CB	Conduction band
CO ₂	Carbon dioxide
CCC	Circumscribed design
CCD	Central composite design
CCF	Faced centered design
CCI	Inscribed design
CVD	Chemical vapor deposition
DOE	Design of experiment
FT-IR	Fourier transform infrared spectroscopy
HCl	Hydrochloric acid
HPLC	High pressure liquid chromatography
H ₂ O	water
H ₂ O ₂	Hydrogen peroxide
KBr	Kalium bromide
NaOH	Sodium hydroxide
N ₂	Nitrogen gas
NPIS	National Pollutant Inventory Substance
O ₂	Oxygen
•OH	Hydroxyl radicals
PEG	Polyethylene glycol
SEM	Scanning Electron Microscope

SNTZS	immobilized nano-TiO ₂ /ZSM-5/silica gel
TEM	Transmission Electron Microscope
TiO ₂	Titanium dioxide
TTIP	Titanium (IV) isopropoxide
UV	Ultra-violet
VB	Valence band
XRD	X-Ray Diffraction

SINTESIS TiO₂-NANO TERSEKAT GERAK UNTUK PENURUNAN FENOL BERFOTOMANGKIN

ABSTRAK

Kehadiran fenol dalam air sisa merupakan permasalahan alam sekitar yang signifikan. Oleh sebab terdapat beberapa kekurangan dalam rawatan air sisa secara konvensional, pemfotomangkinan memberikan alternatif yang menarik. TiO₂-nano tersekat gerak fotomangkin telah berjaya disintesis menggunakan kaedah sol gel terubahsuai dan telah dikaji di dalam reaktor kelompok bagi penurunan fenol berfotomangkin. Komposisi fotomangkin yang telah disintesis ini dibangunkan dengan menggunakan TiO₂-nano sebagai tapak aktif cahaya dan zeolit sebagai bahan penjerap, kesemuanya diikat gerak ke atas sokongan dengan menggunakan pengikat.

Serangkaian percubaan dilakukan untuk mengkaji pengaruh Degussa P25 di dalam sol alkoksida dan jenis yang bersesuaian untuk setiap komponen yang memainkan peranan dalam komponen mangkin TiO₂-nano tersekat gerak. TiO₂ berdasarkan fotomangkin berpenjerap yang mana menggunakan konsep bahan penjerap menumpukan sebatian sasaran berdekatan TiO₂ telah diaplikasikan untuk mengatasi masalah keperluan tenaga yang tinggi akibat aplikasi TiO₂. Tujuan penggunaan mangkin tersekat gerak adalah untuk menghindari keperluan proses pemisahan selepas rawatan yang mahal dan kerana kebolehan mangkin untuk digunakan semula.

Mangkin tersekat gerak dengan jenis setiap komponen yang sesuai dirujuk sebagai TiO₂-nano tersekat gerak/ZSM-5/gel silika (SNTZS). Perumusan optimum mangkin SNTZS telah diamati untuk menjadi (TiO₂-nano: ZSM-5: silika gel: silika gel koloid = 1:0.6:0.6:1) yang mana memberikan kira-kira 90% penurunan daripada

larutan fenol berkepekatan 50 mg /L dalam tempoh 180 minit. SNTZS menunjukkan aktiviti pemfotomangkinan yang lebih tinggi daripada komersil Degussa P25 yang hanya memberikan 67% penurunan. SNTZS fotomangkin yang disintesis dalam kajian ini juga telah terbukti mempunyai lekatan dan kebolehan penggunaan semula yang sangat baik selepas lima kali digunakan semula. SNTZS telah dicirikan dengan menggunakan XRD, SEM, TEM, BET analisis luas permukaan dan FT-IR. Aktiviti pemfotomangkinan yang tinggi mangkin yang disintesis ini adalah disebabkan oleh luas permukaan tertentunya yang besar ($276 \text{ m}^2/\text{g}$), saiz zarah yang kecil (8 – 22 nm) dan kualiti berhablurnya yang tinggi.

Pelbagai parameter operasi seperti kepekatan awal fenol, pH awal dan kepekatan hidrogen peroksida (H_2O_2) telah dikaji. Hasilnya menunjukkan bahawa kadar fotopenurunan berkadar songsang dengan kepekatan awal fenol. Keadaan berasid lebih sesuai bagi penurunal fenol berfotomangkin. Efisiensi penurunan dipertingkatkan dengan penambahan H_2O_2 . Namun, pada kepekatan H_2O_2 yang tinggi (300-500 mg/L), penurunan fenol berkurang kerana pembentukan radikal hiperoksil yang jauh lebih lemah. Keadaan optimum yang dianggarkan adalah pada kepekatan awal fenol 38.43 mg/L, pH awal 3 dan kepekatan H_2O_2 112.67 mg/L, dengan penurunan fenol yang maksima iaitu 97.9 % dalam tempoh sinaran selama 120 minit menggunakan metodologi permukaan respons (RSM). Kinetik bagi penurunan fenol berfotomangkin didapati mematuhi model Langmuir-Hinshelwood.

SYNTHESIS OF IMMOBILIZED NANO-TiO₂ FOR PHOTOCATALYTIC DEGRADATION OF PHENOL

ABSTRACT

The presence of phenol in wastewater represents a significant environmental problem. Due to some drawbacks in conventional wastewater treatment, photocatalysis provides an interesting alternative. Immobilized nano-TiO₂ photocatalyst was successfully synthesized using modified sol gel method and was investigated for photocatalytic degradation of phenol in a batch reactor. The synthesized photocatalyst composition was developed using nano-TiO₂ as photoactive sites and zeolite as adsorbent, all immobilized onto support using binder.

A series of experiments were conducted to investigate the influence of Degussa P25 in alkoxide sol and the suitable type of each component for the role of immobilized nano-TiO₂ catalyst components. TiO₂ based adsorbent photocatalyst which using the concept adsorbent concentrate target compound near TiO₂ was applied to overcome the drawback of the high energy needed of TiO₂ application. The purpose of using immobilized catalyst is to prevent the need of costly separation after treatment and due to the ability of reused catalyst.

The immobilized catalyst with suitable type of each component was referred as immobilized nano-TiO₂/ZSM-5/silica gel (SNTZS). The optimum formulation of SNTZS catalyst was observed to be (nano-TiO₂: ZSM-5: silica gel: colloidal silica gel = 1:0.6:0.6:1) which gave about 90 % degradation of 50 mg/L phenol solution in 180 minutes. The SNTZS exhibited higher photocatalytic activity than that of the

commercial Degussa P25 which only gave 67 % degradation. The SNTZS photocatalyst synthesized in this study was also proven to have an excellent adhesion and reusability after the fifth time of reuse. The SNTZS was characterized using XRD, SEM, TEM, BET surface area analysis and FT-IR. Its high photocatalytic activity was due to its large specific surface area ($276 \text{ m}^2/\text{g}$), small particle size (8 – 22 nm) and high crystalline quality of the synthesized catalyst.

Various operating parameters such as initial phenol concentration, initial pH and hydrogen peroxide (H_2O_2) concentration were examined. The results showed that the photodegradation rate is inversely proportional to initial phenol concentration. Acidic condition was favourable for photocatalytic degradation of phenol. The degradation efficiency is enhanced by addition of H_2O_2 . However, at high concentration of H_2O_2 (300-500 mg/L), phenol degradation decreased due to the formation of a much weaker hydroxyl radical. The optimum conditions were estimated to be 38.43 mg/L of initial phenol concentration, 3 of initial pH and 112.67 mg/L of H_2O_2 concentration, for maximum predicted phenol degradation, 97.9 % in 120 minutes using response surface methodology (RSM). The kinetics of photocatalytic degradation of phenol followed Langmuir-Hinshelwood model.

CHAPTER ONE

INTRODUCTION

As a result of increasing industrialization and the rapid growth of population throughout the world, especially in the last few decades, the quality of our environment deteriorates dramatically. The fast expansion of human activities especially in the industrial activities leads to the water, air and soil pollution. The remediation of hazardous materials in water has attracted great attention in recent years since most of them are soluble in water. Water is the most precious natural resource since it comprising over 70 % of the earth's surface. The organic compounds include phenolic compounds, dye stuff consisting complicated aromatic rings, petroleum products such as oil and gasoline, pesticides, solvents and cleaning agents. In this research, organic compound concerned is phenol as this substance possesses very serious health effects. Development a wastewater treatment system which capable of diminishing the concentration of this toxic and non-biodegradable substance is needed in order to counterbalance these growing environmental problems. Figure 1.1 shows the water cycle in the world.

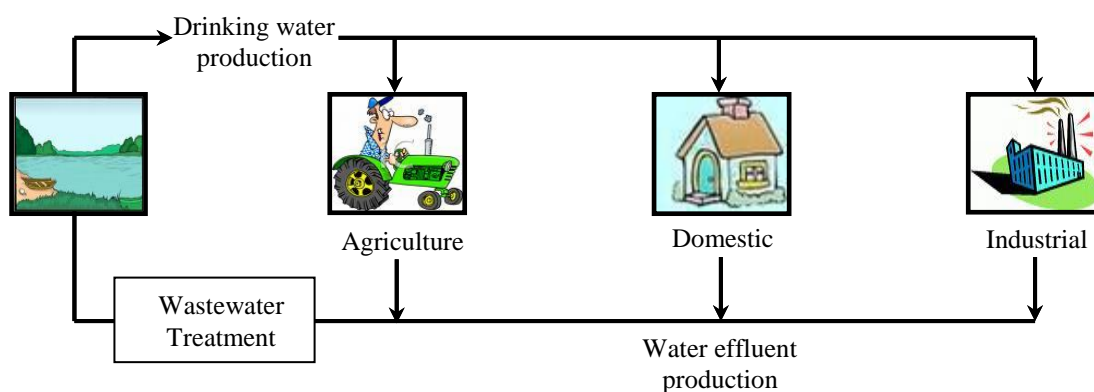


Figure 1.1. A simplified view of the water cycle

1.1 Phenol

Phenol is a significant threat to the environment. It is a specific type of semi-volatile organic compound. Phenol is easily adsorbed by animals and human through the skin and mucous membrane (Abdullah *et al.*, 2006). There are various organizations and ministries that carry out the testing for water quality have imposed strict limits to phenol concentration in industrial discharge. In Malaysia, the Environmental Quality Act and Regulations 1974 has recognized the guidelines limitation for phenol discharges into inland waters is as low as 0.001 mg/L for standard A, 0.1 mg/L for standard B and 5.0 mg/L for other than standard A and B type of industries (MDC, 2000). United States Environmental Protection Agency (USEPA) reported that phenol constitutes 11th of the 126 chemicals which have been pointed as priority pollutants and is listed among the 25 most commonly organics found in groundwater at hazardous waste sites (Abdul Rahim *et al.*, 2003).

1.1.1 Physical and chemical properties of phenol

Phenol is a colourless or a white solid when it is in pure form. However, it generally sold and used as a liquid. Phenol is also known as carbolic acid, phenylic acid, hydroxybenzene, phenic acid and phenyl alcohol (Phenol, 2009). It has relatively high water solubility and quite flammable. Phenol has a characteristic of a typical pungent sweet, medicinal or tar-like odor. The physical properties of phenol are summarized in Table 1.1 (Busca *et al.*, 2008; National Pollutant Inventory Substance Profile, 2009).

Table 1.1. The physical of phenol (Busca *et al.*, 2008; National Pollutant Inventory Substance Profile, 2009)

Properties	Values
Molecular weight (g/mol)	94.11
Boiling point (°C)	181.75
Melting point (°C)	40.9
Auto ignition temperature (°C)	715
Flash point (°C)	79 (closed cup)
Solubility in water (r.t.)	9.3 g _{phenol} /100mL _{H₂O}
Vapour pressure (mm Hg)	0.36 @ 20 °C
pKa	9.89
Flammability Dipole moment (debyes) limits in air (vol %)	1.7 (lower) 8.6 (higher)

According to Busca *et al.* (2008), phenol was first isolated from coal tar in 1834 by the German chemist Runge. It is an aromatic alcohol with a molecular formula of C₆H₅OH. Phenol is the simplest member of the phenolic chemical. Phenol contains a six-membered aromatic ring, bonded directly to a hydroxyl group (-OH) as illustrated in Figure 1.2.

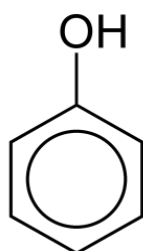


Figure 1.2. Molecular structure of phenol (Busca *et al.*, 2008)

1.1.2 Phenol industrial application and sources

Currently, the world production of phenol is about six million tons per year. Phenol is used as a general disinfectant (household disinfectants, disinfectant soap and handwashes), as an internal antiseptic and gastric anesthetic in veterinary

medicine, as a peptizing agent in glue, as an extracting solvent in refinery and lubricant production, as a blocking agent for blocked isocyanate monomers and as a reagent in chemical analysis. It is also used in the production of fertilizers, explosives, paints and paints removers, drugs, textiles, pharmaceuticals, surfactants, curing agents and so on. Phenol is used primarily as a chemical intermediate in the production of phenolic resins which are low-cost and versatile resins used in the plywood adhesive, construction, automotive, and appliance industries. It is also used as a chemical intermediate in the synthesis of bisphenol A which is used mostly in the manufacture of polycarbonate plastics and epoxy resins and caprolactam which is used in the synthesis of nylon 6 and other synthetic fibers (National Pollutant Inventory Substance Profile, 2009).

Phenol in the aquatic environment can arise from natural sources such as lignin transformation, hydrolysable tannins and flavanoids, algal secretion and humification processes at low concentration (Agarry *et al.*, 2008). However, at high concentrations, it can be found in agricultural activities and some industrial wastewater discharge such as coal gasification, resin manufacturing, oil refining, coking plants, chemical synthesis, dyes, plastics, textiles, detergents, pharmaceuticals, paper mill, agricultural run-off and chemical spills (Chiou and Juang, 2007; Lin and Juang, 2009; Wang *et al.*, 2009c). Table 1.2 shows the concentration of phenol from different industrial wastewater.

Table 1.2. The concentration of phenol in wastewater industries (Veeresh *et al.*, 2005; Jusoh and Razali, 2008; Priya *et al.*, 2008)

Industry	Concentration of phenol (mg/L)
Coal mining	1000-2000
Lignite transformation	10000-15000
Gas production	4000
Petrochemicals	50-700
Pharmaceuticals	1000
Oil refining	2000-20000
Low temperature carbonization	9250-17500
Plastics manufacturing	600-2000
Stocking production	6000

1.1.3 Hazards of phenol

Phenol is considered toxic for some aquatic life even at low concentration (concentrations greater than 50 µg/l) and the ingestion of one gram of phenol can have fatal consequences in humans (Seetharam and Saville, 2003). Oral exposure to phenol becomes the greatest risk to human due to its low volatility affinity for water (Prpich and Daugulis, 2005). Phenol has acute and chronic effects on human health (National Pollutant Inventory Substance Profile, 2009). The acute health effects are increasing respiration rate, followed by a decreasing respiration rate, decreasing body temperature, cyanosis, muscular weakness, weak or occasionally rapid pulse and coma. Effects from chronic exposure to phenol include vertigo, digestive difficulties, skin eruptions, nervous problems and headaches. Phenol also can cause paralysis of the central nervous system and damages the kidney, liver and pancreas (Manahan, 2005; Bólado *et al.*, 2008; Hameed and Rahman, 2008). Death may occur when liver, kidney or pancreas problems become severe.

Another additional effect is the capacity of phenols to combine with existing chlorine in drinking water, giving rise to chlorophenols, compounds that are even more toxic and difficult to eliminate (Chiou and Juang, 2007). So an effective and economic treatment for eliminating phenols in water has been an urgent demand.

1.2 Advanced oxidation processes (AOPs)

Referring to the information cited in Section 1.1.3, presence of phenol in the wastewater obviously can cause various adverse effects on human and environment. Therefore, the wastewater must be treated before discharged to the water stream. Consequently, control of phenol and other pollutant in wastewater has become increasingly stringent all over the world. Amongst the many abatement strategies known, advanced oxidation processes (AOPs) have been a subject of vigorous academic research.

AOP refers to a set of chemical treatment procedures designed including the application of ozone, hydrogen peroxide, ultraviolet light and catalyst, either individually or in combination to remove organic and inorganic materials in waste water by oxidation (Rauf and Ashraf, 2009). The AOP appears as the most emerging promising technologies since it is successfully decompose many hazardous chemical compounds to harmless products such as CO₂ and H₂O, without producing additional hazardous by-products or sludge which require further handling (Molinari *et al.*, 2006; Liotta *et al.*, 2009).

AOPs involve the generation and use of the hydroxyl radical, to destroy compound that cannot be oxidized by conventional oxidants such as oxygen, ozone and chlorine. The relative oxidation potentials of some oxidizing species are listed in Table 1.3. The hydroxyl radical typically attacks organic species by abstracting a hydrogen atom or by adding to the double bond of unsaturated molecules (Hernandez *et al.*, 2002). The hydroxyl radical is a powerful, non-selective oxidant that reacts extremely fast with various compounds until they were completely mineralized. The reactions are able to operate at normal temperature and pressure.

Table 1.3. The relative oxidation potentials of various oxidizing agents (Tchobanoglous *et al.*, 2003)

Oxidizing agent	Electrochemical oxidation potential (EOP), V	EOP relative to chlorine
Fluorine	3.06	2.25
Hydroxyl radical	2.80	2.05
Atomic oxygen	2.42	1.78
Ozone	2.08	1.52
Hydrogen peroxide	1.78	1.30
Hypochlorite	1.49	1.10
Chlorine	1.36	1.00
Chlorine dioxide	1.27	0.93
Molecular oxygen	1.23	0.90

Common AOPs that have been studied in the pollutant treatment processes are photocatalysis, photo oxidation using hydrogen peroxide/ultraviolet light or ozone/UV system, Fenton-type reactions, hydrogen peroxide/ozone, ozone/UV/H₂O₂, and by employing strong oxidants such as ozone at elevated pH (8 to >10). Table 1.4 lists a summary of advantages and disadvantages of the most common AOPs studied in the pollutant treatment process (Asano, 2006).

Table 1.4. A summary of advantages and disadvantages of the most common AOPs studied in the pollutant treatment process (Asano, 2006)

AOPs	Advantages	Disadvantages
Photocatalysis	<ul style="list-style-type: none"> - Greater light transmission achievable after activated with UV light 	<ul style="list-style-type: none"> - Fouling of the UV lamp may occur - Fouling of the catalyst might occur - The catalyst (TiO₂) must be recovered when it was used in a slurry form
Hydrogen peroxide/UV	<ul style="list-style-type: none"> - H₂O₂ is quite stable and can be stored on site temporarily prior to use - 	<ul style="list-style-type: none"> - Special reactors designed for UV irradiation are required - H₂O₂ has very poor UV absorption characteristics and if the water matrix absorbs a lot of UV light energy, subsequently most of the light input to the reactor will be wasted - Fouling of the UV lamp may occur
Ozone/UV	<ul style="list-style-type: none"> - Easier to control ozone dosage - Ozone absorbs more UV light than an equivalent of H₂O₂ dosage 	<ul style="list-style-type: none"> - Special reactors designed for UV irradiation are required - Fouling of the UV lamp may occur - Generation of H₂O₂ by ozone and UV light is inefficient compared to just adding H₂O₂. - Ozone off-gas must be removed
Fenton-type reactions	<ul style="list-style-type: none"> - Some effluents may contain enough Fe to drive the Fenton's reaction - Commercial processes that utilize the technology are available 	<ul style="list-style-type: none"> - Process requires low pH

Table 1.4. Continued

AOPs	Advantages	Disadvantages
H ₂ O ₂ /ozone	<ul style="list-style-type: none"> - Water with poor UV light transmission may be treated - Special reactors designed for UV irradiation are not required 	<ul style="list-style-type: none"> - Generation of ozone can be a costly and inefficient process - Ozone off-gas must be removed - Proper H₂O₂/ozone dosage might be difficult to determine and maintain - Process is harmful at low pH
Ozone/UV/H ₂ O ₂	<ul style="list-style-type: none"> - Commercial processes that utilize the technology are available - H₂O₂ promotes ozone mass transfer 	<ul style="list-style-type: none"> - Special reactors designed for UV irradiation are required - Fouling of the UV lamp may occur - Ozone off-gas must be removed
Ozone at elevated pH (8 to >10)	<ul style="list-style-type: none"> - UV light or H₂O₂ are not required 	<ul style="list-style-type: none"> - Ozone off-gas must be removed - pH adjustment may not be practical

Among the listed AOPs, a great deal of attention has been devoted to photocatalysis since this process resulted in enhanced biodegradability of effluent and achieve reduction in the toxicity with low operation temperature, low cost and significantly low energy consumption (Wang, 2006; Lam *et. al.*, 2008).

1.3 Photocatalysis

Photocatalysis is basically defined as the acceleration of a photoreaction in the presence of a catalyst. The principle of photocatalytic reaction is relatively simple. When a photoactive semiconductor is illuminated by light energy greater than its band gap, pairs of electrons and holes were generated. Some electrons, e⁻, are

excited from the valence band (VB) to the conduction band (CB), leaving positive holes (h^+), in the valence band as illustrated in Figure 1.3. The photoexcited electron and photoexcited hole can be made available to reduce (Pathway a) and oxidize (Pathway b) respectively chemical species on the surface of the photocatalyst, unless they recombine either on the surface of the semiconductor (Pathway c) or in the bulk volume (Pathway d) to give no net chemical reaction but heat.

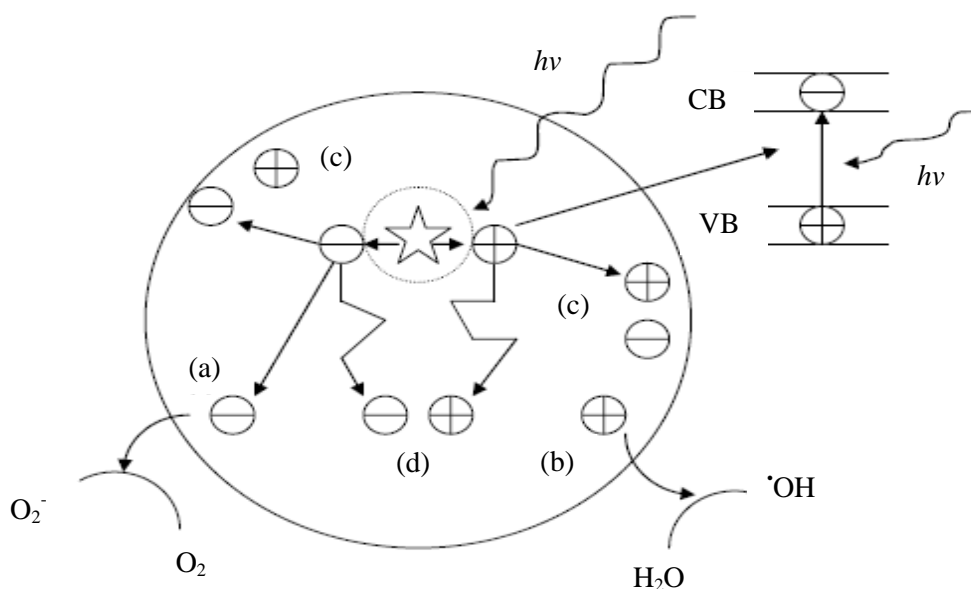


Figure 1.3. Schematic representation of the processes occurring in and on a semiconductor particles following electronic excitation (Hoffman *et al.*, 1995). (a) reduction of O_2 by an electron, (b) oxidation of H_2O by electron hole, (c) and (d) recombination of $e^- h^+$.

1.4 Problem statement

Wastewater derived from different chemical industries such as resin manufacturing, petrochemical, oil-refineries, paper making, textile dyeing and iron smelting has high concentration of phenols and their derivatives such as chlorinated phenolic compounds, which are extremely toxic, carcinogenic and refractory in nature. The permissible concentration of phenol in non-chlorinated water is 0.1 mg/l while that in chlorinated water is 0.001-0.002 mg/l (Gonzalez-Munoz *et al.*, 2003). Thus, the control of phenol in wastewater has become an issue of great importance to

governmental regulatory agencies and general public due to their negative effect towards the environment and human health. The need to the abatement of this pollutant creates a high demand for the technical solution that can meet the environmental regulations and are economically attractive as well. Currently, the utilization of titanium dioxide in photocatalysis area has received considerable attention due to its high efficiency in removing and mineralizing various organic pollutants (Shankar *et al.*, 2006; Yang *et al.*, 2006a; Venkatachalam *et al.*, 2007a; Navio *et al.*, 2008). However, this technology is undergoing some limitations such as requirement of high energy due to low levels of intrinsic quantum yields of titania. Therefore, lately attention has been given to the development of TiO₂ based adsorbent photocatalyst which using the concept of adsorbent concentrate target compounds near TiO₂ to overcome the drawback of the high energy needed (Haque *et al.*, 2005; Tanaka *et al.*, 2006; Mahalakshmi *et al.*, 2009; Yamaguchi *et al.*, 2009) . The second problem arising from this suspension system is it may cause the turbidity in the downstream and further will cause the decrease in depth of UV penetration (Ling *et al.*, 2004). Besides, the obligation to separate the small TiO₂ particles from the suspension after treatment limits the process development. Hence, to overcome the above problems, immobilization is suggested in the waste water treatments (Gelover *et al.*, 2004; Behnajady *et al.*, 2008). Immobilized nano-TiO₂ catalysts can offer high efficiency combined with the ability of photocatalyst to be recycled and reused. The better recovery property is an essential aspect of the cost effectiveness in every process.

1.5 Research objectives

The main objective of this study is to prepare highly active integrated immobilized nano-TiO₂ photocatalyst adsorbent. At the same time, the study aims to achieve the following objectives.

1. To investigate the effects of catalyst components, including adsorbent, support and binder, the effect of each component loading towards degradation of phenol in a batch reactor.
2. To examine the physical and chemical properties of catalyst prepared by performing various characterizations.
3. To evaluate the performance of the best catalyst developed for the photocatalytic degradation of phenol in the batch reactor under a wide range of process parameters, including initial phenol concentration, initial pH and H₂O₂ concentration.
4. To analyze and optimize this process with respect to the simultaneous effects of these parameters on phenol degradation by employed the response surface methodology.
5. To perform kinetic study of photocatalytic degradation of phenol in the batch reactor over the best catalyst prepared in this work.

1.6 Scope of study

The present study mainly focuses on catalyst development, process study as well as kinetic study for the immobilized nano-TiO₂ photocatalyst. Since phenol can cause chronic effects on human and some aquatic life, therefore, in this study phenol is used as the model organic pollutant. As mentioned in Section 1.2., a great deal of

attention has been devoted to advanced oxidation process especially photocatalysis since it can achieves complete oxidation of organic compounds to harmless product such as CO₂ and H₂O. For that reasons, this study is only limited to a photocatalytic degradation of phenol over immobilized nano-TiO₂.

In this study, immobilized nano-TiO₂ is prepared using a base composition (reference composition) of nano-TiO₂:zeolite adsorbent:support:binder=1:1:1:2 (w/w) which 0.25 g TiO₂ is used in 500 mL phenol (0.5 g/L TiO₂). The addition of Degussa P25 is varied from 5 to 30 g/L to evaluate the influence of Degussa P25 in alkoxide sol (modified sol-gel nano-TiO₂). Different types of each component was tested in photocatalytic degradation of phenol by varies one component of the immobilized nano-TiO₂ catalyst while the other components are fixed as reference composition. In this study, ZSM-5 and Zeolite Y represent the type of adsorbent, silica gel and quartz sand represent the type of support, while the type of binder is represented by colloidal silica gel and polyvinyl alcohol. The investigation of optimum immobilized nano-TiO₂ catalyst is then carried out in order to minimize the excess of catalyst.

The optimum composition of immobilized nano-TiO₂ is characterized using X-ray diffractometer (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM), Brunauer-Emmett-Teller surface area analyzer (BET) and Fourier transform infrared spectrometer (FT-IR). In the process study, the effects of initial phenol concentration (25 – 500 mg/L), initial pH (3 – 11) and H₂O₂ concentration (10 – 500 mg/L) are investigated over the optimum immobilized nano-TiO₂ catalysts on photocatalytic degradation of phenol. Data analysis is further

studied using central composite design (CCD) of response surface methodology (RSM) to analyze the influences of each process variable and their interaction effects on phenol degradation. This is followed by the determination of the optimum operating conditions from the set of experimental data collected. Lastly, kinetic study is carried out to determine the rate of reaction. Kinetic model based on the Langmuir Hinshelwood model could be used and the kinetic parameters will be determined.

1.7 Organization of the thesis

This thesis consists of five chapters. Chapter 1 (Introduction) presents a brief description of phenol and its harmful effects, an overview of advanced oxidation processes and a brief introduction of photocatalysis. This chapter also includes the problem statement that provides some basis and rationale on the problems faced and the necessity of the current research. This is followed by the objectives of the study. In the last section of this chapter, the organization of the thesis is presented.

Chapter 2 (Literature Review) presents the information of the past research work regarding this study such as properties of photocatalyst, type of catalysts, effect of process parameters and kinetics study. Some other background information about specific problems that have to be addressed in this research work and the experimental design and methods that are relevant to this research are also provided in this chapter.

Chapter 3 (Materials and Methods) elaborates in details the materials and chemicals used and the research methodology of the present study. Detailed experimental setup including catalyst preparations and process conditions is

described and shown in this chapter. This followed by the discussion of the characterization tools and the statistical design of experiment used.

Chapter 4 (Results and Discussion) is the main part of the thesis and consists of six main sections based on the findings obtained from the current research work. The main topics in this chapter include preliminary study of phenol photodegradation, effect of the catalyst preparation, optimum catalyst characterization, effect of process parameters, optimization process and kinetic study.

Chapter 5 (Conclusions and Recommendations) summarizes the results reported throughout the present study and provides recommendations for future studies in this field.

CHAPTER TWO

LITERATURE REVIEW

This chapter reviews background information on conventional wastewater treatments, the photocatalysis process and TiO₂ photocatalyst. Some other background information about specific problems that have to be addressed in this research work is also provided in this chapter. Finally, the experimental design, method and concept that are being used in this study are presented.

2.1 Conventional Wastewater Treatment

Organic pollutant such as phenol in industrial wastewater effluent is receiving more interest due to its toxicity and difficulty to degrade. Treatment of industrial wastewater can be achieved by physical, chemical and biological unit processes. Conventional wastewater treatment techniques include activated carbon adsorption, chemical oxidation, biological treatment, solvent extraction, etc. have been used to treat different wastewaters contaminated with organic compounds (Chiou and Juang, 2007; Venkatachalam *et al.*, 2007c; Wang *et al.*, 2009c). However, the effectiveness of these processes has become limited due to some increase in the number of industries and subsequently the overall increase in hazardous organic contaminants in the waste stream (Saritha *et al.*, 2007; Laoufi *et al.*, 2008).

These water treatments often transfer one phase to another phase and hence generate large amount of solid wastes. In addition, these processes cannot totally remove organic contaminants and produce hazardous by-products. Subsequently,

costly disposal or regeneration method is required (Villacres *et al.*, 2003; Senthilkumar *et al.*, 2006; Venkatachalam *et al.*, 2007c).

Biological treatment is often not convenient for treatment of phenolic wastewater as its toxicity may cause the phytotoxic effect on the active microorganisms method (Robert and Malato, 2002). All of these conventional wastewater treatments which are currently in use, have drawbacks of their own such as discussed earlier, thus researchers had shifted their attention to advanced oxidation process (AOP) which can achieve complete oxidation of organic compounds to harmless products such as CO₂ and H₂O (Molinari *et al.*, 2006; Saritha *et al.*, 2007; Liotta *et al.*, 2009).

2.2 The photocatalysis process

As reported in earlier chapter, photocatalysis has been shown to be an effective means of treating wastewater effluent containing phenols rather than conventional treatment method (Robert and Malato, 2002). The detail of the advantages of photocatalysis is described as follow:

- (i) The photocatalysis could achieve complete mineralization of organic materials by converting them to carbon dioxide, water and mineral acid.
- (ii) The photocatalysis is able to operate at or slightly above ambient conditions.
- (iii) The photocatalysis allow destruction of non-biodegradable refractory contaminants.

Table 2.1 shows the list of aqueous organic compounds that can be degraded by photocatalysis.

Table 2.1. Organics compounds that can be degraded by heterogeneous photocatalysis

Class of organics	Examples	References
Alkanes	Propane, n-butane, isobutane, heptane, cyclohexane	Li <i>et al.</i> , 2003; Xie <i>et al.</i> , 2004a; Ciambelli <i>et al.</i> , 2005; Twesme <i>et al.</i> , 2006
Haloalkanes	Bromomethane, chloromethane, 1,2-dichloroethane, 1,10-dichlorodecane	El-Morsi <i>et al.</i> , 2000; Yamashita <i>et al.</i> , 2000; Calza and Pelizzetti, 2001; Huang <i>et al.</i> , 2008
Aliphatic alcohols	Methanol, ethanol, 2-propanol, octanol, sucrose, glucose, fructose	Kwon <i>et al.</i> , 2000; Yamashita <i>et al.</i> , 2000; Guillard <i>et al.</i> , 2002; Vorontsov and Dubovitskaya, 2004; Tao <i>et al.</i> , 2006; Teoh <i>et al.</i> , 2007
Aliphatic carboxylic acids	Formic, oxalic acid	Harada and Tanaka <i>et al.</i> , 2006; Mrowetz and Selli, 2006; Karunakaran <i>et al.</i> , 2009
Alkenes	Propene, cyclohexene	Einaga <i>et al.</i> , 2002; Lillo-Rodenas <i>et al.</i> , 2007; Bouazza <i>et al.</i> , 2009
Haloalkenes	Perchloroethene, 1,2-dichloroethylene, trichloroethylene	Hegedus and Dombi, 2004; Ozaki <i>et al.</i> , 2004; Ou and Lo, 2007
Aromatics	Toulene, benzene, naphthalene	Kwon <i>et al.</i> , 2000; Xie <i>et al.</i> , 2004a; Zhang <i>et al.</i> , 2006; Lair <i>et al.</i> , 2008; Tomasic <i>et al.</i> , 2008
Phenolic compounds	Phenol, hydroquinone, cathecol, resorcinol, o-,m- cresol, 4-nitrophenol, 2,4-dinitrophenol, 2,4,6-trinitrophenol	Pal <i>et al.</i> , 2001; Ksibi <i>et al.</i> , 2003; Hatipoglu <i>et al.</i> , 2004; Grzechulska-Damszel <i>et al.</i> , 2006; Tachikawa <i>et al.</i> , 2006; Gummy <i>et al.</i> , 2008

Table 2.1 Continued

Class of organics	Examples	References
Halophenols	4-fluorophenol, 4-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, pentachlorophenol, ,	Essam <i>et al.</i> , 2007; Selvam <i>et al.</i> , 2007, Yang <i>et al.</i> , 2007a
Amines	Alkylamines, alkanolamines, N-nitrosodimethylamine	Klare <i>et al.</i> , 2000; Lee <i>et al.</i> , 2005a
Amides	Benzamide, propyzamide	Robert <i>et al.</i> , 2004; Yano <i>et al.</i> , 2005
Aromatic carboxylic acids	Benzoic, 4-hydroxybenzoic, phthalic, salicylic, phenoxyacetic, 2,4,5-trichlorophenoxyacetic acid	Taborda <i>et al.</i> , 2001; Robert <i>et al.</i> , 2004; Adan <i>et al.</i> , 2006; Kamble <i>et al.</i> , 2006; Singh <i>et al.</i> , 2007; Gumy <i>et al.</i> , 2008; Velegraki and Mantzavinos, 2008
Herbicides	Atrazine, bentazon, isoproturon, simazine, propazine, prometryn	McMurray <i>et al.</i> , 2006; Toepfer <i>et al.</i> , 2006; Evgenidou <i>et al.</i> , 2007; Chu <i>et al.</i> , 2009; Jain <i>et al.</i> , 2009; Pourata <i>et al.</i> , 2009
Pesticides	Lindane, DDT, methoxychlor, pyridaben, terbufos, monocrotophos	Zaleska <i>et al.</i> , 2000; Quan <i>et al.</i> , 2003; Shankar <i>et al.</i> , 2004a; Shankar <i>et al.</i> , 2004b; Zhu <i>et al.</i> , 2004; Wu <i>et al.</i> , 2009
Polymers	Poly-(n-butyl methacrylate), poly-(isopropyl methacrylate), poly-(ethyl methacrylate), poly-(methyl methacrylate), poly-(vynil pyrrolidone)	Horikoshi <i>et al.</i> , 2001; Marimuthu and Madras, 2007
Dyes	Basic Violet 3, Methyl Red, Reactive Yellow 17, Remazol Black 5, Procion Red MX-5B	Gupta <i>et al.</i> , 2006; Rupa <i>et al.</i> , 2007; Sahel <i>et al.</i> , 2007

The photocatalytic reaction can be described as a sequential reaction pathway which has been exhaustively described in the literature. The including steps are listed as follow (Fogler, 1999):

- (i) Mass transfer of reactants from fluid bulk to the catalyst surface (external diffusion);
- (ii) Mass transfer of reactants from the catalyst surface into its pore structure (internal diffusion);
- (iii) Adsorption of reactants;
- (iv) Surface reaction;
- (v) Desorption of products;
- (vi) Mass transfer of products out of the pore structure of the catalyst to the surface;
- (vii) Mass transfer of products from the catalyst surface to fluid bulk.

Photocatalysis process predominantly occurs on the surface of semiconductor. During the photocatalysis process, the suitable light irradiation upon a semiconductor particle activates the catalyst, establishing a redox environment in the aqueous solution (Schiavello, 1985). Hence, photocatalytic reactions (equivalent to step (iv) above) can be explained as follows (Schiavello, 1988, Lam *et al.*, 2008):

- (i) Photogeneration of electron-hole pairs by exciting a semiconductor with radiation of light with energy equal to or higher than its band gap energy;
- (ii) Separation of electron-hole pairs by traps which have a charge carrier trapping rate higher than the charge carrier recombination rate;

- (iii) Redox reaction between the generated charge carriers and adsorbed substrates on the semiconductor surface.

The overall process of the photocatalysis process is described in details in the following section.

2.2.1 Photocatalysis mechanism

Photocatalysis is attributed to the electrical characteristics of semiconductor, which in other word, semiconductor can act as sensitizers for light-induced redox processes. In particular, it is characterized by a filled band (valence band) and an empty band (conduction band) (Wang *et al.*, 2004). The energy difference between these bands, valence and conduction band, is called the band gap. Figure 2.1 shows the schematic diagram of the overall process of semiconductor photocatalysis (Ban *et al.*, 2003).

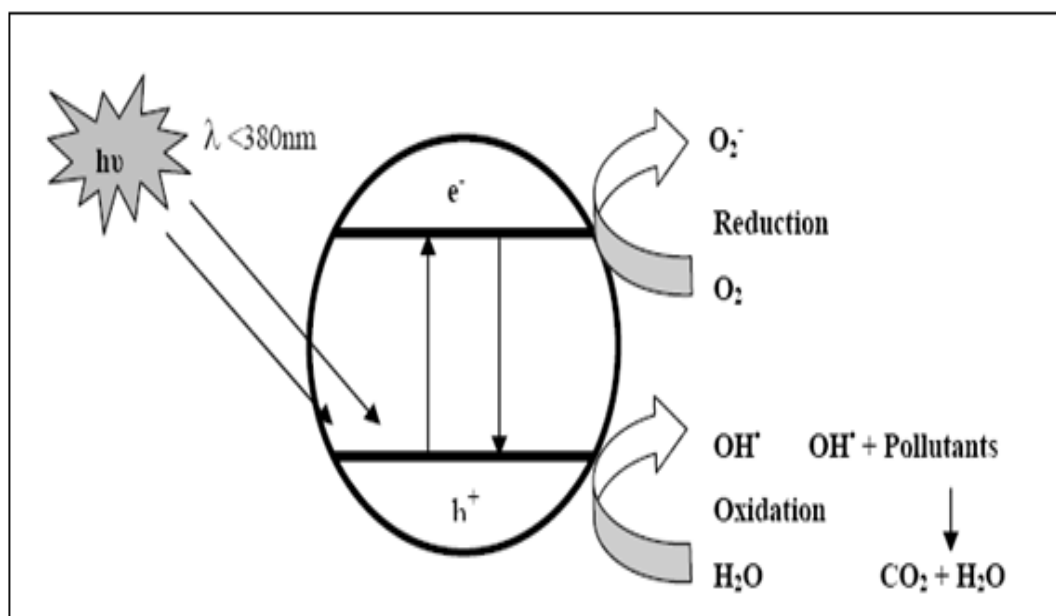


Figure 2.1. Schematic diagram of the overall process of semiconductor photocatalysis (Ban *et al.*, 2003).

When the semiconductor photocatalyst is illuminated with light photon with sufficient energy (energy at or greater than the band-gap energy), will lead to electron excitation, resulting in the generation of an electron-hole pair in the semiconductor particle. As illustrated in Figure 2.1, excited electrons and created holes can undergo different paths (Ban *et al.*, 2003):

- (i) They can get trapped, either in shallow traps (ST) or in deep traps (DT).



e_{tr}^- and h_{tr}^+ correspond to the trapped electron and hole, respectively.

- (ii) They can recombine and dissipating the input energy as heat.
 (iii) They can react with electron donors and acceptor species adsorbed on the semiconductor surface.

The photocatalysis process can also be expressed as a series of complex reaction when taking into account the interactions between the generated charge carriers and adsorbed pollutant molecules onto the photocatalyst surface. Table 2.2 demonstrates the primary processes and characteristic time of photocatalysis on TiO₂ (Hoffmann *et al.*, 1995).

Table 2.2. Primary processes and characteristic time of photocatalysis on TiO₂ (Hoffmann *et al.*, 1995).

Primary process	Equation	Characteristic time (second)
Charge carrier generation		
	$TiO_2 \xrightarrow{h\nu} h_{VB}^+ + e_{CB}^-$	2.3 10^{-15} (very fast)
$OH^{\bullet+}$ formation at the TiO ₂ surface		
	$h_{VB}^+ + >Ti^{IV}OH \rightarrow \{>Ti^{IV}OH^{\bullet+}\}^+$	2.4 10^{-15} (very fast)
Electron trapping		
	$e_{CB}^- + >Ti^{IV}OH \leftrightarrow \{>Ti^{III}OH\}$	2.5 10^{-10} (shallow trap; dynamic equilibrium)
	$e_{CB}^- + >Ti^{IV} \rightarrow >Ti^{III}$	2.6 10^{-8} (deep trap; irreversible)
Charge-carrier recombination		
	$e_{CB}^- + \{>Ti^{IV}OH^{\bullet+}\}^+ \rightarrow >Ti^{III}OH$	2.7 10^{-7} (slow)
	$h_{VB}^+ + \{>Ti^{III}OH\} \rightarrow >Ti^{IV}OH$	2.8 10^{-9} (fast)
Interfacial charge transfer		
	$\{>Ti^{IV}OH^{\bullet+}\}^+ + Red \rightarrow >Ti^{IV}OH + Red^{\bullet+}$	2.9 10^{-7} (slow)
	$e_{tr}^- + O_x \rightarrow >Ti^{IV}OH + O_x^{\bullet+}$	2.10 10^{-3} (very slow)

where;

$>TiOH$ = primary hydrated surface functionality of TiO₂

e_{CB}^- = conduction band electron

e_{tr}^- = trapped conduction band electron

h_{VB}^+ = valence band hole

Red = electron donor (reductant)

O_x = electron acceptor (oxidant)

$\{>Ti^{IV}OH^\bullet\}^+$ = surface trapped VB hole (i.e., surface bound hydroxyl radical)

$\{>Ti^{III}OH\}$ = surface trapped CB electron

Based on the above mechanism, the competition between charge carrier recombination and charge carrier trapping, followed by the competition between trapped carrier recombination and interfacial charge transfer are two critical processes which determine the overall quantum efficiency for interfacial charge transfer (Hoffmann *et al.*, 1995). The decrease in the charge carrier recombination is expected to cause increase in quantum efficiencies.

2.2.2 Semiconductor photocatalyst

Semiconductor is a material that has electrical conductivity between that of a conductor and an insulator. The studies on semiconductors as a kind of photocatalyst, for environmental clean up have receive significant interest from many researchers since 1970s (Feng and Nansheng, 2000; Hashimoto *et al.*, 2005). Various metal oxides (i.e. TiO_2 , ZnO , MoO_3 , CeO_2 , ZrO_2 , WO_3 and SnO_2) and metal chalcogenides (i.e. ZnS , CdS , $CdSe$, WS_2 and MoS_2) are used as photocatalysts. Table 2.3 shows the redox potentials of some common semiconductor (Robertson, 1996). In the past 20 years, researchers have studied on the modification of these semiconductors in order to improve the activity and catalyst efficiency of photocatalyst and to degrade effectively all kinds of organic substances in water and air under certain light. (Grzechulska-Damszel *et al.*, 2006, Janus *et al.*, 2009). However, a lot of interest have addressed to the utilization of TiO_2 and modified TiO_2 as a semiconductor for