UNIVERSITI PUTRA MALAYSIA

SYNTHESIS OF TiO_2 AND Fe_2O_3-DOPED TiO_2 FOR PHOTOCATALYTIC DEGRADATION OF 2,4-DICHLOROPHENOXYACETIC ACID

AFINI BINTI RAZANI

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By

AFINI BINTI RAZANI

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science

April 2015

This thesis dedicated to:
My beloved parents,
my other half,
&
family.

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Master of Science

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Chair: Associate Professor Abdul Halim Abdullah, PhD
Faculty: Science

2,4-Dichlorophenoxyacetic acid (2,4-D), a widely used herbicide for selective control of broadleaf weeds which has been detected as a major contaminant in surface or underground water since its degradation in water is very slow, with half-life ranging from 4 to7 days in most soil types and up to 6 weeks in acidic soils. The TiO_2, 0.025%, 0.05% and 0.1% Fe_2O_3 doped TiO_2 were synthesized via co-precipitation method, calcined at 550°C and used as photocatalyst to photodegrade 2,4-D in aqueous solution. The synthesized metal oxides were then characterized by X-Ray Diffractometer (XRD), X-Ray Fluoresence (XRF), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Band Gap, and Brunauer, Emmet and Teller (BET) surface area analysis. All catalysts exhibited spherical anatase TiO_2 phase. With the addition of Fe_2O_3, the surface area, particle size and band gap energy were lower than undoped TiO_2. When comparing the photocatalytic activity of TiO_2 and Fe_2O_3 doped TiO_2, 0.05% Fe_2O_3 doped TiO_2 was found to give the highest degradation (33.1%). This may attributed to its small particle size (12.67 nm) and low band gap energy (~3.07). Conventional method and Response Surface Methodology (RSM) with a Face-Centred Central Composite Design (FCCCD) was used to optimize the photocatalytic degradation of 2,4-D using 0.05% Fe_2O_3 doped TiO_2 as catalyst. The optimum conditions for photocatalytic degradation of 2,4-D using 0.05% Fe_2O_3 doped TiO_2 were predicted at 10 mg/L of initial concentration of 2,4-D, 1.0 g of mass loading of 0.05% Fe_2O_3 doped TiO_2 and initial 2,4-D pH of 4.0 with a predicted percentage of degradation of 45.24%. The model was validated and the result showed no significant difference between the experimental and the predicted percentage of degradation. The photocatalytic efficiency of the catalyst remained unchanged after the first cycles of photodegradation experiments which indicate the stability of the catalyst until the fifth cycle.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Sarjana Sains

SINTESIS TiO_2 DAN Fe_2O_3 DIDOPKAN TiO_2 UNTUK FOTOKATALITIK DEGRADASI 2,4-DIKLOROFENOKSIASETIK ASID

Oleh

AFINI BINTI RAZANI

April 2015

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Asid 2,4-diklorofenoksiasetik (2,4-D) adalah racun tumbuhan yang digunakan secara meluas untuk pengawalan terpilih rumpai berdaun lebar dan telah dikesan sebagai pencemar utama dalam air di permukaan atau bawah tanah kerana penguraian 2,4-D di dalam air adalah sangat perlahan, dengan jangka separuh hayat adalah di antara 4 hingga 7 hari dalam kebanyakan jenis tanah dan sehingga 6 minggu dalam tanah berasid. TiO_2 dan Fe_2O_3 didopkan TiO_2 telah disintesis melalui kaedah ko-pemendakan, dikalsin pada suhu 550°C dan digunakan sebagai fotopemangkin untuk fotodegradasi 2,4-D dalam larutan akueus. Logam oksida kemudian dicirikan dengan Sinar-X Difraktometer (XRD), Sinar-X Pendarfluor (XRF), Mikroskop Pengimbasan Elektron (SEM), Transmisi Mikroskop Elektron (TEM), Julang Tenaga, dan luas permukaan Brunauer, Emmet dan Teller (BET). Semua mangkin menunjukkan fasa sfera anatasa TiO_2. Dengan penambahan Fe_2O_3, luas permukaan, saiz zarah dan julang tenaga adalah lebih rendah berbanding TiO_2. Apabila aktiviti fotopemangkinan antara TiO_2 dan Fe_2O_3 didopkan TiO_2 dibandingkan, 0.05% Fe_2O_3 didopkan TiO_2 didapati mempunyai aktiviti penyingkiran tertinggi (33.1%). Hal ini disebabkan oleh saiz partikel yang kecil (12.67 nm) dan julang tenaga yang rendah (~3.07). Cara konvensional dan Metodologi Respon Permukaan (RSM) digunakan untuk mengoptimumkan degradasi fotokatalitik 2,4-D menggunakan 0.05% Fe_2O_3 didopkan TiO_2 sebagai mangkin. Keadaan optimum untuk degradasi fotopemankinan 2,4-D menggunakan 0.05% Fe_2O_3 didopkan TiO_2 telah dianggarkan pada 10 mg/L kepekatan awal larutan 2,4-D, 1.0 g jisim mangkin 0.05% Fe_2O_3 didopkan TiO_2 dan pH awal larutan 2,4-D adalah 4.0 dengan peratusan degradasi yang diramalkan adalah 45.24%. Model ini adalah sahih dan hasilnya tidak menunjukkan perbezaan yang signifikan antara hasil eksperimen dan peratusan jangkaan degradasi. Kecekapan fotopemangkin kekal tidak berubah selepas kitaran pertama eksperimen fotopemangkinan menunjukkan mangkin ini stabil sehingga kitaran kelima.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

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Declaration by Members of Supervisory Committee

This is to confirm that:

- the research conducted and the writing of this thesis was under our supervision;
- supervision responsibilities as stated in the Universiti Putra Malaysia (Graduate Studies) Rules 2003 (Revision 2012-2013) are adhered to.

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LIST OF ABBREVIATIONS

~	approximately
°	Degree
°C	degree Celsius
$\bullet O_2^-$	super radical or super Oxide
$\bullet OH^-$	hydroxyl radical
2,4-D	2,4-dichlorophenoxyacetic Acid
3D	Three Dimension
Å	Armstrong
ANOVA	Analysis of Variance
AOP	Advanced Oxidation Process
BET	Brunauer, Emment, and Teller
BJH	Barrett, Joyner, and Halender
C_0	initial concentration
CCD	Central Composite Design
C_t	concentration at time
df	degree of freedom
e^-	electron
E_{bg}	band gap energy
eV	electroVolt
FCCCD	Face Centered Central Composite Design
Fe_2O_3	Ferum Oxide
g	gram
gL-1	gram per liter

h^+	hole
JCPDS	Joint Committee on Powder Diffraction Standards
k_1	first-order rate constant
kV	kilo Volt
LOF	Lack of Fit
M	Molarity
min	minutes
nm	nanometer
p/p_0	relative pressure
ppm	part per million
r	rate of reaction
R^2	correlation factor
	coefficient of determination
RSM	Response Surface Methodology
SC	Semiconductor
SEM	Scanning Electron Microscope
$t_{1/2}$	half life
TEM	Transmission Electron Microscope
TiO_2	Titanium Dioxide
UV	Ultra Violet
XRD	X-Ray Diffractometer
XRF	X-Ray Fluorescence
λ	wavelength
ϕ_{ions}	ionic fraction

CHAPTER 1

INTRODUCTION

Water is an important element for all forms of life. Most living organisms can survive only for short duration without water as water is an essential resource that sustains living things on earth. Water pollution has become one of the major world problems that may lead to diseases and death. Wastewater and organic pollutants such as dyes and phenolic compounds are harmful to our surrounding environment and human due to its low biodegradability. Nowadays, human create and dispose excessive wastewater and organic pollutants along with the rapid industrial development. Therefore, the unwanted constituent mostly can be found in the industrial effluent (Fernández et al., 2010).

It is known that 2,4-Dichlorophenoxyacetic acid (2,4-D) is a widely used herbicide in modern cultivation for selective control of broadleaf weeds. This herbicide is more preferable to be used due to its low cost and good selectivity (Hameed et al., 2009). However, the degradation of 2,4-D in water is very slow, with half-life ranging from 4–7 days in most soil types, for example, approximate 6 weeks in acidic soils (Toft, 2003). It has been detected as major contaminant in surface or underground water (Alvarez et al., 2007). Despite its short half-life in soil or aquatic environments, this herbicide is considered to be potentially hazardous to humans and animals, toxicological studies shows that it posseses a great potential for inducing undesirable effects affecting non-targeted organisms (Alexandre et al., 2007). Therefore, several studies such as adsorption (Bohli et al., 2013; Hameed et al., 2009), solvent extraction (Wang et al., 2014), radiation (Rauf & Ashraf, 2009), chemical oxidation, reverse osmosis (Otake et al., 2009), chlorination (Ge et al., 2008), membrane process (Harrelkas et al., 2009) and biodegradation (Kumar et al., 2013) had been applied to remove this type of contaminant in the effluent.

These methods are expensive or have drawbacks due to the propensity to secondary toxic materials (Liotta et al., 2009). Alternatively, advanced oxidation process (AOP) is a suitable method to be used as it is able to degrade organic pollutants to harmless and lower molecular weight products such as CO_2 and H_2O. Among AOPs, heterogeneous photocatalysis has become the main attention due to the capability and efficiency of this method in removing organic compounds (Umar & Aziz, 2013). This method is considered as cost-effective as the required treatment reagents are easily available and the involved operating techniques and conditions are simple.

Photocatalysis using suspended semiconductor catalyst is a common way to degrade various types of organic and inorganic pollutants in waste water hence preserving the environment (Lezner et al., 2012; Zhan et al., 2011). Semiconductor catalysts such as TiO_2, ZnO, Fe_2O_3, CdS, GaP and ZnS are widely used due to their degradation efficiency and the probability of the formation of secondary toxic materials is rather low and they are ultimately mineralized to harmless product (CO_2 and H_2O) (Chong et al., 2010). TiO_2 has been widely used as photocatalyst in degrading water pollutants due to its high reactivity under the photon energy of 300 nm < λ < 390 nm (Malato et al., 2009), lower toxicity, thermally and chemically stable of even after several cycles of reaction, and it is cost-effective (Choi, 2006; Fujishima et al., 2000).

TiO_2 have huge applications in industries such as in air purification system for air pollutant removal, water purification, electrical appliances, paints, cosmetics like sun blocks, removal of residual pesticides and herbicides in agriculture field, energy conversion of solar cells and water splitting application (Nakata & Fujishima, 2012). TiO_2 can be prepared by various methods like sol-gel (Akpan & Hameed, 2011), hydrothermal (Vijayalakshmi & Rajendran, 2012), spray-pyrolysis (Li et al., 2005; Ye & Ohmori, 2002), flame synthesis (Yang et al., 2003), chemical-vapour deposition (Li et al., 2002), precipitation (Chen et al., 2010; Li et al., 2009) and others. Different preparation of catalysts may lead to various characteristics of products such as specific surface areas, porosities and surface compositions (Dauscher et al., 1992). In this study, precipitation method is chosen to prepare the catalyst as this method is simple and easy to be conducted in the laboratory.

The photocatalytic degradation process is influenced by several parameters such as mass of the catalyst, concentration of the pollutants as well as pH of the pollutant solutions. In this study, response surface methodology (RSM) was applied in the process of parameters optimization in order to investigate the interaction between the degradation process and the observable parameters. RSM is a collection of mathematical and statistical techniques for designing experiments, building model and evaluating the effect of factors (Bezerra et al., 2008). The data collected are analyzed using analysis of variance (ANOVA), while the optimal values of the operation parameters are estimated based on the polynomial regression equation, and three dimensional (3D) response surface analysis graphs (Zhang et al., 2010).

1.1 Problem Statements

The applications of TiO_2 are limited due to several reasons. Firstly, TiO_2 has low photon quantum efficiency resulting from the recombination of photogenerated electron-hole pairs (Kokila et al., 2011; Zhao et al., 2011). Secondly, the photocatalytic efficiency of TiO_2 is not high since it is only active under ultraviolet (UV) light (Zhan et al., 2011).

In order to overcome these problems, the catalyst can be modified by incorporating transition metals into the original system. Among various types of investigated dopants, Fe_2O_3 is the best candidate because of the ionic radius of Fe^{3+} is similar to Ti^{4+} which are 0.64 Å and 0.68 Å respectively (Ranjit & Viswanathan, 1997). Due to its low band gap energy (~2.3 eV) (Yalçın et al., 2010), Fe^{3+} ion may act to reduce the band gap energy of TiO_2 and improve the charge separation of the electron-hole pairs, and this helps in enhancing the photoactivity (Ranjit & Viswanathan, 1997). Besides, TiO_2 that was doped with Fe^{3+} has a profound effect on the charge carrier recombination (Djerdj & Tonejc, 2006).

Optimization of the photodegradation process is always performed based one factor at a time while keeping other parameters constant level. This optimization technique is called one-variable-at-a-time. The disadvantage of this technique is the interaction effect does not include among the variables studied. So, this technique does not show the complete effect of the parameter on the response. The other disadvantage of one-variable-at-a-time technique is the number of experiment conducted is numerous thus will lead to increment of the utilization of time, expenses, reagents and materials (Bezerra et al., 2008). Thus, this limitation can be solved by applying response surface methodology that has the capability to evaluate the relationship between the variables and the responses. The influence responses of each single variable or parameter can be determined by the combination of experiments through this application (Zafari, 2013).

It is hoped that this work may provide a driving force in incorporating Fe_2O_3 dopant into TiO_2 catalyst as a potential catalyst in degrading several organic pollutants besides of 2,4-D pollutant. Through this work, it is also hoped that response surface methodology (RSM) could be recognized as an alternative way to determine the optimization of parameters that may help in reducing waste chemicals which could save our world from chemical contaminations.

1.2 Scope of Research

In this research work, TiO_2 and Fe_2O_3 doped TiO_2 catalyst were synthesized using precipitation method. The amount percentage of Fe_2O_3 dopant was varied from 0.025%, 0.05% and 0.1% for synthesis of Fe_2O_3 doped TiO_2.

In order to give a better understanding, various characterizations, especially on the physicochemical properties were conducted on the synthesized catalysts. They were characterized by using X-Ray diffractometry (XRD), X-Ray fluorescence (XRF), scanning electron microscopy (SEM), transmission electron microscopy (TEM), band gap analysis, Brunauer, Emment and Teller (BET) surface area and pH for point of zero charge.

The efficiency of photocatalytic activity of TiO_2 and Fe_2O_3 doped TiO_2 were evaluated by degrading 2,4-Dichlorophenoxyacetic acid (2,4-D). The degradation were examined using UV-Vis spectrophotometer by determining the initial and final concentrations of the 2,4-D pollutant. The effects of operational parameters were carried out using conventional and response surface methodology methods to determine the optimum conditions for catalyst loading, initial concentration and initial pH of 2,4-D solution. The significant differences between these two methods also were evaluated. Lastly, from the obtained optimum parameters, the reusability test for the optimum catalyst was carried out to investigate the efficiency of the catalyst.

1.3 Research Objectives

The main objective of this study is to synthesize an efficient photocatalyst for photodegradation of 2,4-D. Thus, the objectives throughout this study are as follows:

i. To synthesize and characterize TiO_2 and Fe_2O_3 doped TiO_2 photocatalysts.

ii. To evaluate the photocatalytic activity of the synthesized catalyst in degrading 2,4-D as pollutant.

iii. To optimize the conditions for degradation of 2,4-D using response surface methodology.

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