

SYNTHESIS AND CHARACTERIZATIONS OF ZnO AND ITS DOPED
NANOPARTICLES VIA SOL-GEL METHOD FOR PHOTOCATALYTIC
DEGRADATION OF ENVIRONMENTAL POLLUTANTS
UNDER DIRECT SOLAR RADIATION

MUNEER MOHAMMED AWADH BAABBAD

THESIS SUBMITTED IN FULFILMENT OF THE DEGREE OF
DOCTOR OF PHILOSOPHY

FACULTY OF ENGINEERING AND BUILT ENVIROMENT
UNIVERSITI KEBANGSAAN MALAYSIA
BANGI

2014

**SINTESIS DAN PENCIRIAN ZnO DAN NANOPARTIKEL YANG DIDOP
MELALUI KAEDAH SOL-GEL UNTUK PENGURAIAN FOTOPEMAN-
GKINAN BAHAN PENCEMAR ALAM SEKITAR DI BAWAH
SINARAN MATAHARI SECARA LANGSUNG**

MUNEER MOHAMMED AWADH BAABBAD

**TESIS YANG DIKEMUKAKN UNTUK MEMPEROLEH IJAZAH
DOKTOR FALSAFAH**

**FAKULTI KEJURUTERAAN DAN ALAM BINA
UNIVERSITI KEBANGSAAN MALAYSIA
BANGI**

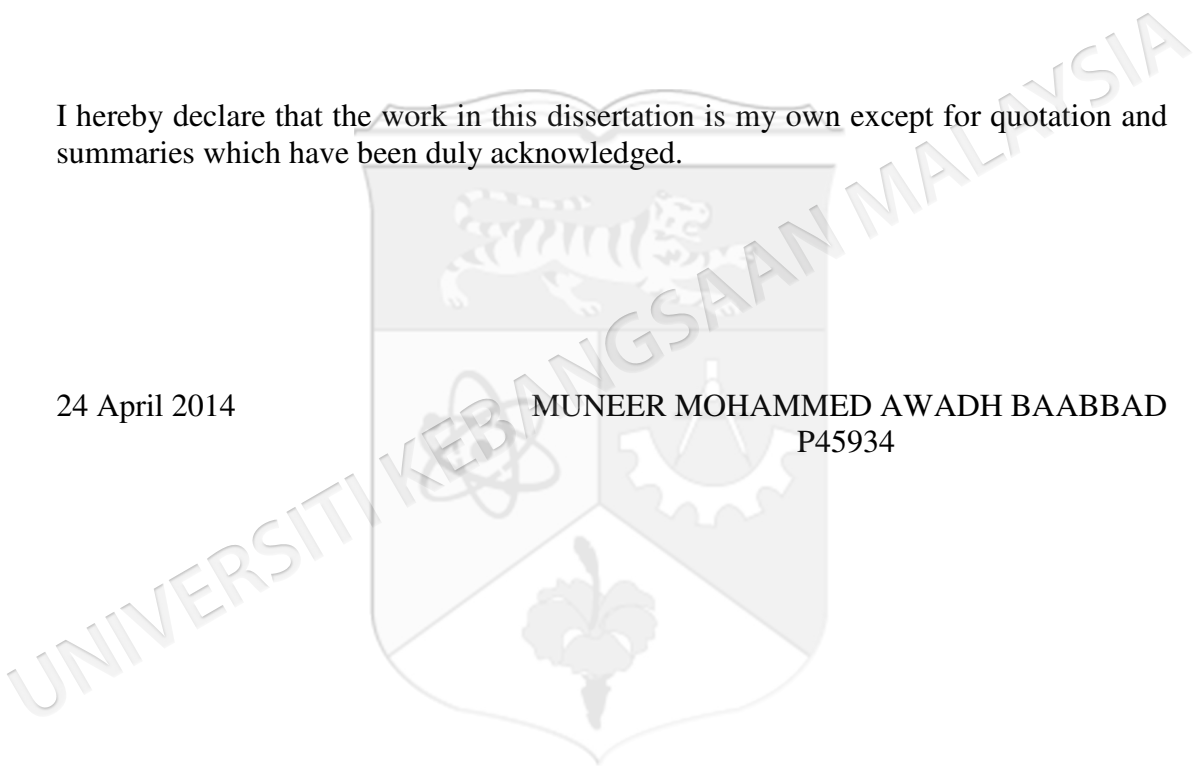
2014

DECLARATION

I hereby declare that the work in this dissertation is my own except for quotation and summaries which have been duly acknowledged.

24 April 2014

MUNEER MOHAMMED AWADH BAABBAD
P45934



ACKNOWLEDGEMENT

First and foremost praise to Almighty Allah for all his blessings for giving me patience and good health throughout the duration of this PhD research. I am very fortunate to have Prof. Dr. Abdul Amir H. Kadhum for his guidance throughout the duration of the PhD study. I am very grateful for his financial support for all analysis of my samples. I would like to express my high appreciation to my co-supervisor Prof. Dr. Abu Bakar Mohammad for his time to guide me and his advices for academic guidance within my study. Also, I would like to thank Prof. Dr. Mod Sobri Takriff for his advices about the overall my thesis outline and his appreciate advices. Moreover, I am grateful to Prof. Dr. Kamaruzzaman Sopian for his great helping for supporting of solar intensity instruments.

I would like to thank all members of Chemical and Process Engineering Department for all of their support and friendship within my study period. At same time, I would like to thanks a lot for the analysis laboratory in Chemical and Process Engineering Department for their friendship, and creating a pleasant working environment throughout my years in UKM. I gratefully acknowledge financial support provided by UKM under grant numbers UKM-DLP-2011-064 and UKM-DIP2012-02. Also, I would like to acknowledge to my friend from Faulty of science and technology, school of applied physics, UKM for his great helping about analysis.

Last but not least, greatest thankful to my family and my university in Yemen, Hadhramout University of Science and Technology who given me tremendous support this study.

ABSTRACT

ZnO nanoparticles (ZnO NP) have been found to be excellent materials for photocatalysis process in the environmental purification of toxic organic pollutants due to its good optical and chemical properties as well as its low cost. Many earlier studies have made use the capping agent or a surfactant to control the size of the semiconductor nanoparticles. Most of the capping agent comprise of toxic chemicals, which are difficult to be removed from the surface of the synthesized nanoparticles apart from contaminating the environment and add cost for scale up production. Hence, this research aimed to synthesize the ZnO NP using sol-gel method without using capping agent or surfactant to control the particle size. In addition, the effects of process parameters, namely, molar ratio, pH and calcination temperatures on the synthesis and the characterizations of ZnO NP have also been investigated. The optimization of process parameters for synthesis of ZnO NP was performed using Response Surface Methodology technique (RSM). In order to improve the properties of ZnO NP, doping with transition metal ions using iron (Fe^{3+}), titanium (Ti^{4+}) and samarium (Sm^{3+}) were also carried out. The activity of both, ZnO and its doped NP, was then examined for the photodegradation of polychlorinated phenol. Finally, the mechanism and toxicity of polychlorinated phenol degradation before and after degradation were determined. ZnO NP and its doped catalysts were synthesized using sol-gel method, in which gel solutions containing zinc acetate and oxalic acid with different molar ratios were added in ethanol with water using various selected pHs. The ZnO gel and doped ZnO NP were dried and calcined at different temperatures of 400, 500 and 600 °C, then characterized using selected instrumental measurements. A cylinder batch reactor with continuous stirring was used to investigate for photodegradation of polychlorinated phenol under direct solar radiation energy. For the photodegradation experiments, 2-level factorial and RSM were selected for conducting the survey and optimization. Five parameters, namely, loading, pH, calcination temperature, concentration and solar intensity were investigated in this study. The degradation efficiency and mechanism were evaluated using HPLC and GC-MS, whereas the toxicity was tested using *Escherichia coli* bacteria with inhibition zone method. The experimental optimum condition of molar ratio of 1.76, pH of 1.50 and calcination at 402.2 °C produced ZnO NP with particle size of 18 ± 2 nm compared with 22.9 nm from model. The study on the effects of process parameters on the morphological and optical properties of ZnO NP showed increased in size of ZnO NP and formation of larger agglomeration when the molar ratio, pH and calcination temperature were in within the optimal condition. The surface area and optical properties were found to be improved by doping the catalyst. The optimal concentration for dopant was found at 0.5 wt. % for Fe^{+3} and Sm^{+3} , and 0.25 wt. % for Ti^{+4} . The optimal condition for photodegradation was found at pH of 6.09, calcination temperature of 411.50 °C with solar intensity of 23 W/m^2 with the efficiency of 97.80 % which was in close agreement with the experimental of 99.54 %. The comparison between the activity of ZnO and its doped NP for photodegradation showed that the efficiency increased up to one and a half times for doped compared to undoped ZnO NP under the same experimental conditions. The intermediate compound produced from degradation of polychlorophenols was nontoxic as shown via the toxicity study.

ABSTRAK

Nanopartikel ZnO (ZnO NP) dicirikan sebagai pemangkin-cahaya yang baik dalam proses penulenan sebatian organik bertoksik disebabkan oleh optiknya dan ciri-ciri kimia yang baik serta menjimatkan. Hasil kajian awal menunjukkan agen penutup atau surfaktan digunakan untuk mengawal saiz nanopartikel semikonduktor. Kebanyakan agen penutup mengandungi bahan kimia bertoksik yang sukar untuk disingkirkan daripada permukaan nanopartikel yang disintesis dan ia juga meningkatkan kos bagi pengeluaran skala naik. Justeru itu, kajian ini adalah bertujuan untuk mensintesis ZnO NP menggunakan kaedah sol-gel tanpa menggunakan agen penutup atau surfaktan untuk mengawal saiz zarah. Kajian kesan parameter proses iaitu nisbah molar, pH dan suhu pengkalsinan terhadap sintesis dan pencirian ZnO NP turut dijalankan. Pengoptimuman parameter proses untuk sintesis ZnO NP telah dijalankan menggunakan kaedah sambutan permukaan (RSM). Bagi meningkatkan ciri-ciri ZnO NP, pengedopan dengan ion logam peralihan seperti besi (Fe^{3+}), titanium (Ti^{4+}) dan samarium (Sm^{3+}) telah dijalankan. Seterusnya, aktiviti ZnO dan ZnO NP yang didop dianalisis untuk penguraian foto sebatian fenol berpoliklorin. Akhirnya, mekanisme dan kajian ketoksikan penguraian sebatian fenol berpoliklorin sebelum dan selepas penguraian telah ditentukan. ZnO NP dan pemangkinnya yang didop telah disintesis menggunakan kaedah sol-gel, yang mana larutan sol-gel yang mengandungi zink asetat dan asid oksalik dengan nisbah molar yang berbeza ditambah dalam etanol dengan pH air yang pelbagai. Gel ZnO dan ZnO NP yang didop kemudian dikeringkan dan dikalsinkan pada suhu 400, 500 dan 600 °C dan dicirikan menggunakan teknik ukuran yang berbeza. Reaktor berjujukan silinder dengan pengadukan yang berterusan telah digunakan untuk mengkaji penguraian foto sebatian fenol berpoliklorin di bawah sinaran matahari secara langsung. Bagi kajian penguraian foto, kaedah faktorial dua peringkat dan RSM telah digunakan untuk mengoptimumkan lima parameter proses termasuk suapan organik, pH, suhu pengkalsinan, kepekatan dan keamatan sinaran. Kecekapan penguraian dan mekanisme telah dianalisis dengan HPLC dan GC-MS, manakala ketoksikan telah diuji menggunakan bakteria *Escherichia-coli* dengan kaedah zon perencatan. Keadaan optimum kajian pada nisbah molar 1.76, pH 1.50 dan suhu pengkalsinan 402.2 °C menghasilkan ZnO NP bersaiz 18 ± 2 nm berbanding 22.9 nm dari model. Kajian kesan parameter proses terhadap morfologi dan sifat optik ZnO NP menunjukkan saiz ZnO NP meningkat dan pengumpulan yang lebih besar terhasil apabila nisbah molar, pH dan suhu pengkalsinan adalah di antara keadaan optimum. Luas permukaan dan sifat-sifat optik telah meningkat dengan menggunakan proses pengedopan mangkin. Kepekatan optimum untuk bahan dop adalah pada 0.5% berat bagi Fe^{+3} dan Sm^{+3} manakala 0.25% berat bagi Ti^{+4} . Keadaan optimum untuk penguraian foto telah ditemui pada pH 6.09, suhu pengkalsinan 411.50 °C dan keamatan sinaran 23 W/m² dengan kecekapan sebanyak 99.54 % yang menghampiri dengan nilai 97.80 % daripada model teori. Sebatian perantaraan yang dihasilkan daripada penguraian poliklorofenol adalah tidak toksik seperti yang didapati melalui ujian ketoksikan.

CONTENTS

	Page
DECLARATION	iii
ACKNOWLEDGMENT	iv
ABSTRACT	v
ABSTRAK	vi
CONTENTS	vii
LIST OF TABLES	xiii
LIST OF FIGURES	xvi
LIST OF ABBREVIATIONS	xxii
 CHAPTER I	
INTRODUCTION	
1.1 Research Background	1
1.2 Problem Statment	4
1.3 Research Objectives	6
1.4 Scope of the Study	6
1.5 Thesis Outline	8
 CHAPTER II	
LITRETURE REVIEW	
2.1 Introduction	9
2.2 Properties of ZnO Nanoparticles	11
2.2.1 Mechanical Properties	11
2.2.2 Electronic Properties	11
2.2.3 Optical Properties	11
2.2.4 Magnetic Properties	12
2.2.5 Physical Properties	13
2.3 Synthesis Method of ZnO Nanoparticles	14
2.3.1 Vapor Phase Growth Process	14
2.3.2 Solution phase growth process	16

2.4	Classification of ZnO Nanostructure	19
2.4.1	Zero-Dimensional (0) of ZnO Nanostructure	20
2.4.2	One-Dimensional (1D) of ZnO Nanostructure	20
2.4.3	Two-Dimensional (2D) of ZnO Nanostructure	23
2.4.4	Three-Dimensional (3D) of ZnO Nanostructure	24
2.5	Synthesis Of 0D Of ZnO Nanostructure and Advantages	26
2.5.1	Heightened Surface to Volume Ratio and Catalysis	26
2.5.2	Quantum Size Effects	27
2.5.3	Synthesis of 0D of ZnO Nanoparticles using Sol-gel Technique	27
2.5.4	Effecting Parameters on Sol-Gel Preparation	29
2.5.5	Doping of 0D ZnO Nanoparticles and Their Properties	37
2.6	Application of Nanoparticles Semiconductors for Photocatalysis Process	41
2.6.1	Homogenous Photocatalysis	42
2.6.2	Heterogeneous Photocatalysis	43
2.6.3	Mechanism of Heterogeneous Photocatalysis	44
2.6.4	Factors Affecting on the Photocatalysis Process	47
2.6.5	Surface Morphology and Structural Properties of ZnO	51
2.6.6	Photocatalytic Degradation of Organic Pollutants using ZnO	52
2.7	Design of Experiments (DOE) for ZnO Synthesis and Photocatalysis Application	59
2.7.1	Design of Experiments (DOE)	60
2.7.2	Response Surface Methodology (RSM)	62
2.7.3	Second-order experimental designs	66
2.7.4	RSM Design for Optimization of photocatalytic Process	71

CHAPTER III MATERIALS AND METHOD

3.1	Introduction	78
3.2	Materials	80
3.2.1	Chemicals and Solvent	80
3.2.2	Degradant Compound	80
3.3	Preparation Method of ZnO and Doped Nanoparticles	81

3.3.1	Preparation Procedures and Set-Up	81
3.3.2	Optimization of Process Parameters Using RSM	83
3.3.3	Statistical Analysis of RSM	83
3.4	Doping Of ZnO Nanoparticles by Different Metal Ions	87
3.5	Characterization of ZnO and Doped ZnO Nanoparticles	88
3.5.1	Thermal Analysis	89
3.5.2	X-Ray Diffraction Analysis	89
3.5.3	Field Emission Scanning Electron Microscope	90
3.5.4	Transmission Electron Microscope	90
3.5.5	Brunauer-Emmett-Teller (BET) Surface Area	91
3.5.6	Zeta Potential (Surface Charge)	91
3.5.7	Diffuse Reflectance using UV/Vis Spectrophotometer	92
3.5.8	Atomic Absorption Spectrometer	92
3.6	Application of ZnO Nanoparticles For Chlorophenols Degradation under Solar Radiation	92
3.6.1	Standard of Degradant Compound	93
3.6.2	Experimental Set Up for Solar Photocatalytic Process	93
3.6.3	Effects Parameters Using RSM design	94
3.6.4	Location of Experiments	97
3.7	Experimental Analysis	97
3.7.1	High-Performance Liquid Chromatography	98
3.7.2	Ion Liquid Chromatography	98
3.7.3	Gas Chromatography	98
3.7.4	Chemical Oxygen Demand	99
3.7.5	Toxicity Evaluation	100
3.8	Solar Intensity Measurements	101

CHAPTER IV SYNTHESIS OF ZnO NP AND ITS CHARACTERIZATION

4.1	Introduction	103
4.2	Optimization of ZnO NP	103
4.2.1	Model Fitting of D-optimal Designs	105
4.2.2	Adequacy Check of the Model	107
4.2.3	Response Surface Plotting and Optimization	109
4.2.4	Model Validation and Experimental Confirmation	111
4.2.5	Characterizations of ZnO NP and Comparison	113

4.2.6	Validation of Optimum Condition for Other Metal Oxide	116
4.3	Thermal Analysis	119
4.3.1	Undoped ZnO NP Precursors	119
4.3.2	Doped ZnO Precursors	122
4.4	X-ray Diffraction (XRD) Analysis	125
4.4.1	X-ray Diffraction of ZnO NP	125
4.4.2	X-ray Diffraction of Doped ZnO NP	129
4.5	Surface morphology analysis	135
4.5.1	Surface Morphology of ZnO NP	135
4.5.2	Surface morphology of Doped ZnO NP	142
4.6	Optical properties	147
4.6.1	Optical Properties of ZnO NP	147
4.6.2	Optical Properties of Doped ZnO NP	153
4.7	Surface properties analysis	159
4.7.1	Zero- Point Charge of ZnO NP	159
4.7.2	Zero- Point Charge of Doped ZnO NP	160
4.8	Surface Area Analysis	162
5.7.1	Surface Area of ZnO NP	162
5.7.2	Surface Area of Doped ZnO	165

CHAPTER V

APPLICATION OF ZnO NP IN PHPTOCATALYTIC REACTION

5.1	Introduction	168
5.1.1	Factor Screening for Photocatalytic Experiments	168
5.1.2	Optimization of Photocatalytic Process Using RSM	174
5.2	Application of ZnO and Doped ZnO NP for Degradation of Chlorophenols under Direct Solar Light	185
5.2.1	Effects of Process Parameters on Activity of ZnO NP	185
5.2.2	Effects of Doping on Activity of ZnO NP	202
5.2.3	Toxicity Evaluation of Chlorophenols Degradation	210

5.2.4	Intermediates Compound of Chlorophenols Degradation	213
5.2.5	Performance of ZnO NP Activity for Degradation of Other Pollutants	225

CHAPTER VI CONCLUSION AND RECOMMENDATIONS

6.1	Overall Conclusions	227
6.2	Suggestions for Future Work	230

REFERENCES	231
-------------------	-----

APPANDIXS	259
------------------	-----

A	Published Papers from this Thesis	259
B	Chemical, solvent and degradants properties	263
C	Standard of chlorophenols	266
D	Certificate of <i>E.coli</i> bacteria	269
E	Solar intensity instrument	270
F	TGA-DSC analysis	273
G	Chloride ions concentration (Cl^-)	274
H	Degradation of chlorophenols using doped ZnO	277
I	Atomic absorption spectroscopy analysis	278
J	Determination of intermediate compounds using HPLC	280
K	Structure and molecular weight of intermediates using GC-MS	282

LIST OF TABLES

Table No.		Page
2.1	Physical properties of ZnO	13
2.2	Summary of affect various parameters on sol gel process	33
2.3	Spherical ZnO nanoparticles (0D) synthesized by sol gel method with different conditions	34
2.4	Different doping of ZnO 0D nanoparticles (spherical) synthesis by sol gel method and their properties	39
2.5	Summary of band gap for most applied of semiconductors	43
2.6	Oxidation potential of oxidants	47
2.7	Types of CPs in drinking water	53
2.8	Photocatalytic degradation of various organic pollutants using ZnO with different conditions	56
2.9	Comparison of experiment runs according of number of factors	70
2.10	Optimization of photocatalytic degradation for different pollutants using RSM	73
2.11	Application of D-optimal design on in chromatographic and fluorescence techniques	77
3.1	Parameters and levels of D-optimal design	85
3.2	Experimental runs of D-optimal design	86
3.3	Parameters and their levels of two level full factorial design	95
3.4	Experimental runs of screening using two-level full fractional Design	96
3.5	Parameters and levels for photocatalytic degradation process	96
3.6	Experimental runs of optimization using D-optimal design	97
4.1	Parameters and levels of D-optimal design	104
4.2	Experimental runs of D-optimal design with Actual	105

4.3	ANOVA results for quadratic model of ZnO NP	107
4.4	Optimization of all factors to obtain smaller particle size of ZnO NP	112
4.5	Comparison of ZnO particle size prepared by different methods	115
4.6	Particle size of several metal oxide synthesized by sol gel using optimum conditions of D-optimal design	116
4.7	Weight loss of ZnO and doped ZnO NP precursors temperatures profile	124
4.8	Crystal size and lattice parameters of ZnO and doped ZnO NP with various concentrations of dopants	134
4.9	Comparison of particle size between TEM and XRD under different of experimental conditions	137
4.10	The weight % and atomic % results of ZnO nanoparticle at different conditions	142
4.11	The weight % and atomic % results of doped ZnO NP at optimum concentration	147
4.12	Optical properties of ZnO nanoparticles under different conditions	151
4.13	Band gap comparison of ZnO and doped ZnO NP using different ions and their concentrations	157
4.14	Surface properties of ZnO NP under several condition of preparation	164
4.15	Surface properties of doped ZnO NP with different ions	167
5.1	Photocatalytic degradation parameters and their levels	169
5.2	Response results of screening design using two-level factorial design	170
5.3	ANOVA results for screening using two-level factorial design	170
5.4	Parameters and their levels for optimization of photocatalytic process	174
5.5	Actual and predicted results of optimization based on D-optimal design with DE% and COD % responses	175

5.6	Analysis of variance (ANOVA) for the DE% of 2-CP	178
5.7	Analysis of variance (ANOVA) for the COD % of 2-CP	178
5.8	Experimental run and optimum conditions of all factors under range to maximize DE % and COD % for 2-CP	182
5.9	First-order rate constants (k , min ⁻¹) of chlorophenols at different initial concentrations	198
5.10	Comparison of toxicity of chlorophenols (by mm) before and after degradation time using ZnO and it's doped by Fe ³⁺ ions under optimal concentration.	212
5.11	Comparison of retention time between the HPLC and GC-MS for the chlorophenols and intermediate compounds.	215



LIST OF FIGURES

Figure No.		Page
1.1	Flowchart of overall steps for synthesis and application of ZnO and doped ZnO NPs	7
2.1	Zinc crystal structures: (a) cubic rocksalt, (b) cubic zinc blende, (c) wurtzite hexagonal structure	10
2.2	Hexagonal wurtzite as stable structure of ZnO form	10
2.3	Main methods of ZnO Nanoparticles synthesis	14
2.4	Dimensionality classifications of nanostructured materials	19
2.5	The 0 D TEM images of ZnO nanoparticles prepared by several methods as: (a) Chemical deposition, (b) MVCVD, (c) Pulsed laser ablation, (d) Sonochemical reduction, (e) solvothermal, (f) sol gel, (g) Precipitation, (h) Hydrothermal, (i) Polyol method, (j) CVD	21
2.6	The 1 D SEM images of ZnO nanostructures prepared by several methods as: (a) Pulse laser deposition, (b) Thermal evaporation, (c) MOCVD, (d) CVD (e) Hydrothermal, (f) Sol gel, (g) Microwave, (h) Sonochemical, (i) Electrochemical deposition, (j) Sputtering process	22
2.7	The 2 D SEM images of ZnO nanostructures prepared by several methods as: (a) Nanosheet by Electrochemical, (b) Nanosheet by Sol gel, (c) Nanowall by Thermal evaporation, (d) Nanodisks by Hydrothermal, (e) Nanoplates by Hydrothermal, (f) Nanoflakes by Physical vapor deposition	23
2.8	The 3D SEM images of ZnO nanoparticles prepared by several methods as (a), (b) nanoflowers by sol gel, (c) nanoflowers by microwave, (d) nanotube by electrochemical, (e) nanocone by hydrothermal, (f) nanocone by CVD, (g) nanopillars by MOCVD, (h) nanoballs by sol gel	25
2.9	Principle of surface to volume ratio	26
2.10	Procedures of sol gel process to synthesized of nanoparticles	28
2.11	Flow chart of gel-sol route to prepare the metal oxide	30
2.12	Types of ZnO nanostructure doping, (a) n-type, (b) p-type	37

2.13	Comparison between the photosynthesis and photocatalysis under solar	42
2.14	The solar spectrum and their comparison between UV, and Visible	50
2.15	Comparison of global and direct UV of solar on earth surface	51
2.16	Relationship between the factors and responses within the process	60
2.17	(a) D-optimal algorithm selection (b) D-optimal reduces runs	69
3.1	Shows the overall flow sheet of study procedures	79
3.2	Experimental procedures of ZnO and doped ZnO NPs synthesized by sol gel method	82
3.3	RSM procedures for optimization ZnO NP synthesis process	84
3.4	Batch solar photoreactor (non-concentrating type slurry reactor)	94
3.5	Inhibition zone determination of <i>E.coli</i> bacteria's growth	101
3.6	(a) Solar intensity measurements set up, and (b) Radiometer for determination a total solar radiation	101
4.1	All diagnostic plots of optimization ZnO NP process using D-optimal design, (a) Normality, (b) Studentized residuals, (c) Outlier T, (d) Actual and predicted size of ZnO NP	108
4.2	The effect of the molar ratio, pH and calcination temperature the particle size of ZnO NP for the D-optimal design	110
4.3	Predicted particle size, as obtained from the RSM based on D-optimal design under optimal conditions	112
4.4	ZnO NP characterization (a) XRD pattern of ZnO NP (b)TEM image under optimal conditions of D-optimal design	114
4.5	TEM images for different metal oxide prepared by sol gel under optimum conditions, (a) CuO, (b) α -Fe ₂ O ₃ , (c) Co ₃ O ₄ , (d) TiO ₂ , (e) NiO	117
4.6	XRD patterns of different metal oxide with JCPDS standard prepared by sol gel under optimum conditions, (a) CuO, (b) α -Fe ₂ O ₃ , (c) Co ₃ O ₄ , (d) TiO ₂ , (e) NiO	118
4.7	TGA-DSC spectra for thermal decomposition of zinc oxalate dehydrate, (a) ratio =1:1 at pH of 2.0, (b) ratio = 1:2 at pH of	121

	2.0,(c) ratio = 1:3 at pH of 2.0, (d) ratio = 1:2 at pH of 1.0, (e) ratio = 1:2 at pH of 3.0, (f) ratio = 1:2 at pH of 5.0	
4.8	TGA-DSC curves of (a) undoped ZnO (b) 0.5 wt % Fe^{3+} doped ZnO (c) 0.5 wt % Sm^{3+} doped ZnO (d) 0.5 wt % Ti^{4+} doped ZnO NP sample	123
4.9	XRD analysis of the starting materials and ZnO NP after calcinations	126
4.10	XRD analysis of (a) ZnO NP prepared in different molar ratio, (b) ZnO NP prepared at different pH, (c) ZnO NP at different calcination temperatures	127
4.11	XRD patterns spectrum of (a) Fe^{3+} -doped ZnO NP with different concentration calcined at 400°C (b) shifted of peak (101) position is observable towards to right	130
4.12	XRD patterns spectrum of (a) Sm^{3+} -doped ZnO nanoparticles with different concentration calcined at 400°C (b) shifted of peak (101) position is observable towards to left side	132
4.13	XRD patterns of (a) Ti^{4+} -doped ZnO nanoparticles with different Sm^{3+} concentrations calcined at 400°C (b) no shifting of peak (101) position is observable	133
4.14	FESEM and TEM images of ZnO NP prepared under ratio of Z_{ac}/O_{xa} , (a, a_1) 1:1, (b, b_1) 1:2, (c, c_1) 1:3	136
4.15	FESEM and TEM images of ZnO NP prepared under 1:2 molar ratio and various of pH at (a_2, a_3) 1.0 before washing; (b_2, b_3) 1.0 after washing; (c_2, c_3) 2.0; (d_2, d_3) 3.0; (e_2, e_3) 5.0 ± 0.2	138
4.16	FESEM and TEM images of ZnO NP prepared under 1:2 molar ratio and pH of 2.0 at calcination temperature of (a_4, a_5) 400°C , (b_4, b_5) 500°C , (c_4, c_5) 600°C	140
4.17	EDX of ZnO NP calcined at 400°C with various values of pH, (a) 2.0, (b) 3.0, (c) 5.0 ± 0.2	141
4.18	FESEM and TEM images of (a, a_1) undoped ZnO NP; (b, b_1) 0.5 wt. % of Fe^{3+} ; (c, c_1) 1.00 wt. % of Fe^{3+} doped ZnO NP	143
4.19	FESEM and TEM images of (a, a_1) undoped ZnO; (b, b_1) 0.5 wt. % of Sm^{3+} ; (c, c_1) 1.00 wt. % of Sm^{3+} doped ZnO	144
4.20	FESEM and TEM images of (a, a_1) undoped ZnO; (b, b_1) 0.5 wt.% of Ti^{4+} ; (c, c_1) 1.00 wt.% of Ti^{4+} doped ZnO	145

4.21	Energy dispersive X-ray (EDX) of different dopant into ZnO (a) undoped ZnO; (b) Fe^{3+} ; (c) Sm^{3+} ; (d) Ti^{4+}	146
4.22	Optical properties of ZnO NP under different molar ratio (a) Diffuse Reflectance, (b) Absorbance, (c) Band gap	149
4.23	Diffuse reflectance of the ZnO precursor (a) before calcinations; (b) at 400°C ; (c) 500°C ; (d) 600°C ; (e) ZnO commercial; (f) at pH of 3.0; (g) at pH of 5.0	150
4.24	Absorption spectra of ZnO NP under different of (a) molar ratio, (b) pH and calcination temperatures	152
4.25	Optical properties of Fe^{3+} doped ZnO NP under optimal conditions (a) Diffuse reflectance, (b) Absorbance, (c) Band gap	154
4.26	Optical properties of Sm^{3+} doped ZnO NP under optimal conditions (a) Diffuse reflectance, (b) Absorbance, (c) Band gap	156
4.27	Optical properties of Ti^{4+} doped ZnO NP under optimal conditions (a) Diffuse reflectance, (b) Absorbance, (c) Band gap	158
4.28	Zero point charge (pH_{zpc}) of undoped ZnO NP at different calcination temperatures (a) at 400°C , (b) 500°C , (c) 600°C	160
4.29	Zero point charge (pH_{zpc}) of doped ZnO NP with at different concentration of dopant Fe^{3+} , (b) Sm^{3+} , (c) Ti^{4+}	161
4.30	Nitrogen adsorption-desorption of ZnO NP prepared under different process parameters, (a) molar ratio, (b) pH, (c) calcination temperatures	163
4.31	Nitrogen adsorption-desorption of doped ZnO NP with (a) Fe^{3+} , (b) Sm^{3+} , (c) Ti^{4+} doped ZnO	166
5.1	Some characteristics of the model screening, (a) Normality, (b) Residual. (c) Outlier test, (d) predicated and actual results	171
5.2	Pareto plot for (a) Effect of factors (b) Estimate effects of factors on degradation efficiency	173
5.3	Diagnostic plots of the degradation efficiency for optimization process	177
5.4	Response surface and contours graphs of degradation efficiency (DE %) with affecting of the process factors, (a)	180

	calcintion temperature and pH,(b) solar intensity and pH,(c) solar intensity and calcination temperature	
5.5	Response surface and contours graphs of degradation efficiency (COD %) with affecting of the process factors, (a) calcintion temperature and pH,(b) solar intensity and pH,(c) solar intensity and calcination temperature	181
5.6	Analysis of photocatalytic degradation using HPLC and UV (a) 2-CP before reaction, (b) first run by HPLC,(c) second run by HPLC,(d) first and second run by UV	183
5.7	Analysis of photocatalytic degradation using HPLC under second run condition (a, a ₁) 2,4-DCP, and (b, b ₁) 2,4,6-TDCP before and after degradation	184
5.8	Solar radiation measurements (a) UVA, (b) UVB and (C) Total radiation	187
5.9	Effects of different conditions of solar on degradation efficiency of chlorophenols using initial concentration 50 mg/l, loading of 2 g/l, pH solution at 6.0	188
5.10	Effects of ZnO NP synthesized parameters on degradation efficiency of chlorophenols, (a) molar ratio , (b) pH, (c) calcination temperatures under 60 min irradiation time	189
5.11	Effects of ZnO NP loading on degradation of chlorophenols under pH solution of 6.0, initial concentration of 50 mg/l, and irradiation time of 60 min	191
5.12	Effects of pH solution on the degradation of chlorophenols efficiency under initial concentration of 50 mg/l, irradiation time of 60 min, and loading of 2g/l on sunny day	192
5.13	Comparison of adsorption amount of chlorophenols on surface of ZnO NP under dark condition for 60 min	194
5.14	Photocatalytic degradation of different chlorophenols concentrations under optimum conditions (a) 2-CP, (b) 2,4-DCP, (c) 2,4,6-TCP	196
5.15	The first order reaction of, (a) 2-CP, (b) 2,4-DCP, (c) 2,4,6-TCP	197
5.16	Comparison of COD removal of chlorophenols with different concentrations under same conditions, (a) 2-CP, (b) 2,4-DCP, (c) 2,4,6-TCP	199
5.17	Chloride ions increasing as function of irradiation time for	201

degradation process of chlorophenols

5.18	Comparison between 2-CP, 2,4-DCP and 2,4,6-TCP for chloride ions production within degradation process	202
5.19	Comparison of photocatalytic degradation efficiency (DE %), surface area (SA) and band gap (BG) vs. the different concentration of dopants	204
5.20	Effects of loading on degradation efficiency (DE %) for optimal concentration of Fe^{3+} , Sm^{3+} and Ti^{4+} doped ZnO, with 50 mg/l of 2-CP at pH of 6.0, 60 min irradiation	208
5.21	Effects of initial concentration of chlorophenols on degradation efficiency (DE %) using of Fe^{3+} doped ZnO, (a) 2-CP, (b) 2,4-DCP and (c) 2,4,6-TCP	209
5.22	Toxicity test of chlorophenols before and after degradation using <i>E-coli</i> bacteria, (a) 2-CP before, (b) 2,4-DCP before, (c) 2,4,6-TCP before (a ₁); 2-CP by ZnO, (b ₁) 2,4-DCP by ZnO, (c ₁) 2,4,6-TCP by ZnO; (a ₂) 2-CP by $\text{Fe}^{3+}/\text{ZnO}$, (b ₂) 2,4-DCP by $\text{Fe}^{3+}/\text{ZnO}$, (c ₂) 2,4,6-TCP by $\text{Fe}^{3+}/\text{ZnO}$	213
5.23	GC-MS chromatogram of intermediate compounds within degradation process of (a) 2-CP, (b) 2,4-DCP, (c) 2,4,6-TCP	214
5.24	HPLC chromatogram of degradation of 2-CP under optimum condition using (a) 2-CP before (b) ZnO, (c) $\text{Fe}^{3+}/\text{ZnO}$, (d) $\text{Sm}^{3+}/\text{ZnO}$, (e) $\text{Ti}^{4+}/\text{ZnO}$	216
5.25	GC-MS chromatogram of degradation of 2-CP under optimum condition after 30 min irradiation time (a) 2-CP (b) phenol, (c) catechol, (d) hydroxyhydroquinone (HHQ), (e) 2-chlorohydro-quinone (CHQ), (f) maleic and fumaric acid, (g) Oxalic acid	218
5.26	Path way fragmentation of 2-CP degradation using ZnO and doped ZnO NP under solar light	219
5.27	GC-MS chromatogram of degradation of 2,4-DCP under optimum condition after 30 min irradiation time (a) 2,4-DCP (b) 2-CP (c) phenol, (d) hydroquinone, (e) hydroxyhydroquinone (HHQ), (f) 2-chlorohydroquinone (CHQ), (g) maleic and fumaric acid, (h) Oxalic acid	221
5.28	GC-MS chromatogram of degradation of 2,4,6-TCP under optimum condition after 30 min irradiation time (a) 2,4,6-TCP (b) 2,4-DCP (c) 2-CP (d) phenol, (e) catechol, (f) hydroxyhydroquinone (HHQ), (g) 2-chlorohydroquinone	222

(CHQ),(h) maleic and fumaric acid, (i) Oxalic acid

5.29	Path way fragmentation of 2,4-DCP degradation using ZnO, doped ZnO NP under solar light	223
5.30	Path way fragmentation of 2,4,6-TCP degradation using ZnO and doped ZnO NP under solar light	224
5.31	Photocatalytic degradation of pollutants using ZnO NP under solar light, (a) methyl blue, (b) methyl orange, (c) methyl red, (d) lignin	226



LIST OF ABBREVIATIONS

e^-	Electron
h^+	Hole
$\cdot OH$	Hydroxyl radical
$\cdot O_2^-$	Super oxide radical
β_0	Regression coefficients
X_i	Factor
K	Factor number
y_i	Response
ε	Residual error
α	Optical absorption coefficient
$h\nu$	Photon energy
E_g	Direct band gap
E_d	Constant
N	Experimental runs
B	Vector
C_o	Initial concentration at $t=0$
C	Initial concentration at interval time
k	Constant
t	Time
m/z	Characteristic masses

ABSTRACT

ZnO nanoparticles (ZnO NP) have been found to be excellent materials for photocatalysis process in the environmental purification of toxic organic pollutants due to its good optical and chemical properties as well as its low cost. Many earlier studies have made use the capping agent or a surfactant to control the size of the semiconductor nanoparticles. Most of the capping agent comprise of toxic chemicals, which are difficult to be removed from the surface of the synthesized nanoparticles apart from contaminating the environment and add cost for scale up production. Hence, this research aimed to synthesize the ZnO NP using sol-gel method without using capping agent or surfactant to control the particle size. In addition, the effects of process parameters, namely, molar ratio, pH and calcination temperatures on the synthesis and the characterizations of ZnO NP have also been investigated. The optimization of process parameters for synthesis of ZnO NP was performed using Response Surface Methodology technique (RSM). In order to improve the properties of ZnO NP, doping with transition metal ions using iron (Fe^{3+}), titanium (Ti^{4+}) and samarium (Sm^{3+}) were also carried out. The activity of both, ZnO and its doped NP, was then examined for the photodegradation of polychlorinated phenol. Finally, the mechanism and toxicity of polychlorinated phenol degradation before and after degradation were determined. ZnO NP and its doped catalysts were synthesized using sol-gel method, in which gel solutions containing zinc acetate and oxalic acid with different molar ratios were added in ethanol with water using various selected pHs. The ZnO gel and doped ZnO NP were dried and calcined at different temperatures of 400, 500 and 600 °C, then characterized using selected instrumental measurements. A cylinder batch reactor with continuous stirring was used to investigate for photodegradation of polychlorinated phenol under direct solar radiation energy. For the photodegradation experiments, 2-level factorial and RSM were selected for conducting the survey and optimization. Five parameters, namely, loading, pH, calcination temperature, concentration and solar intensity were investigated in this study. The degradation efficiency and mechanism were evaluated using HPLC and GC-MS, whereas the toxicity was tested using *Escherichia coli* bacteria with inhibition zone method. The experimental optimum condition of molar ratio of 1.76, pH of 1.50 and calcination at 402.2 °C produced ZnO NP with particle size of 18 ± 2 nm compared with 22.9 nm from model. The study on the effects of process parameters on the morphological and optical properties of ZnO NP showed increased in size of ZnO NP and formation of larger agglomeration when the molar ratio, pH and calcination temperature were in within the optimal condition. The surface area and optical properties were found to be improved by doping the catalyst. The optimal concentration for dopant was found at 0.5 wt. % for Fe^{+3} and Sm^{+3} , and 0.25 wt. % for Ti^{+4} . The optimal condition for photodegradation was found at pH of 6.09, calcination temperature of 411.50 °C with solar intensity of 23 W/m² with the efficiency of 97.80 % which was in close agreement with the experimental of 99.54 %. The comparison between the activity of ZnO and its doped NP for photodegradation showed that the efficiency increased up to one and a half times for doped compared to undoped ZnO NP under the same experimental conditions. The intermediate compound produced from degradation of polychlorophenols was nontoxic as shown via the toxicity study.

ABSTRAK

Nanopartikel ZnO (ZnO NP) dicirikan sebagai pemangkin-cahaya yang baik dalam proses penulenan sebatian organik bertoksik disebabkan oleh optiknya dan ciri-ciri kimia yang baik serta menjimatkan. Hasil kajian awal menunjukkan agen penutup atau surfaktan digunakan untuk mengawal saiz nanopartikel semikonduktor. Kebanyakan agen penutup mengandungi bahan kimia bertoksik yang sukar untuk disingkirkan daripada permukaan nanopartikel yang disintesis dan ia juga meningkatkan kos bagi pengeluaran skala naik. Justeru itu, kajian ini adalah bertujuan untuk mensintesis ZnO NP menggunakan kaedah sol-gel tanpa menggunakan agen penutup atau surfaktan untuk mengawal saiz zarah. Kajian kesan parameter proses iaitu nisbah molar, pH dan suhu pengkalsinan terhadap sintesis dan pencirian ZnO NP turut dijalankan. Pengoptimuman parameter proses untuk sintesis ZnO NP telah dijalankan menggunakan kaedah sambutan permukaan (RSM). Bagi meningkatkan ciri-ciri ZnO NP, pengedopan dengan ion logam peralihan seperti besi (Fe^{3+}), titanium (Ti^{4+}) dan samarium (Sm^{3+}) telah dijalankan. Seterusnya, aktiviti ZnO dan ZnO NP yang didop dianalisis untuk penguraian foto sebatian fenol berpoliklorin. Akhirnya, mekanisme dan kajian ketoksikan penguraian sebatian fenol berpoliklorin sebelum dan selepas penguraian telah ditentukan. ZnO NP dan pemangkinnya yang didop telah disintesis menggunakan kaedah sol-gel, yang mana larutan sol-gel yang mengandungi zink asetat dan asid oksalik dengan nisbah molar yang berbeza ditambah dalam etanol dengan pH air yang pelbagai. Gel ZnO dan ZnO NP yang didop kemudian dikeringkan dan dikalsinkan pada suhu 400, 500 dan 600 °C dan dicirikan menggunakan teknik ukuran yang berbeza. Reaktor berjujukan silinder dengan pengadukan yang berterusan telah digunakan untuk mengkaji penguraian foto sebatian fenol berpoliklorin di bawah sinaran matahari secara langsung. Bagi kajian penguraian foto, kaedah faktorial dua peringkat dan RSM telah digunakan untuk mengoptimumkan lima parameter proses termasuk suapan organik, pH, suhu pengkalsinan, kepekatan dan keamatan sinaran. Kecekapan penguraian dan mekanisme telah dianalisis dengan HPLC dan GC-MS, manakala ketoksikan telah diuji menggunakan bakteria *Escherichia coli* dengan kaedah zon perencatan. Keadaan optimum kajian pada nisbah molar 1.76, pH 1.50 dan suhu pengkalsinan 402.2 °C menghasilkan ZnO NP bersaiz 18 ± 2 nm berbanding 22.9 nm dari model. Kajian kesan parameter proses terhadap morfologi dan sifat optik ZnO NP menunjukkan saiz ZnO NP meningkat dan pengumpulan yang lebih besar terhasil apabila nisbah molar, pH dan suhu pengkalsinan adalah di antara keadaan optimum. Luas permukaan dan sifat-sifat optik telah meningkat dengan menggunakan proses pengedopan mangkin. Kepekatan optimum untuk bahan dop adalah pada 0.5% berat bagi Fe^{+3} dan Sm^{+3} manakala 0.25% berat bagi Ti^{+4} . Keadaan optimum untuk penguraian foto telah ditemui pada pH 6.09, suhu pengkalsinan 411.50 °C dan keamatan sinaran 23 W/m² dengan kecekapan sebanyak 99.54 % yang menghampiri dengan nilai 97.80 % daripada model teori. Sebatian perantaraan yang dihasilkan daripada penguraian poliklorofenol adalah tidak toksik seperti yang didapati melalui ujian ketoksikan.

CHAPTER I

INTRODUCTION

1.1 RESEARCH BACKGROUND

Nanotechnology is a well-known term for many applications using nano-scale items for specific procedures. It is defined as the synthesis, characterization and application of material science that has dimensions on a nanometer scale (Daniel & Astruc 2003). During the last two decades, the application of nanotechnology has developed to cover multi-scientific fields such as drug development, water decontamination, and human health care. Water and air are vital for the continued existence of mankind as these are vital elements in the metabolic processes of the human body. As such, the contamination of these elements poses a serious threat to public health in the form of diseases including cancer. Decontamination methods such as physical, chemical neutralization and detoxification technologies using nano-materials have been applied for the removal or reduction of organic pollutants (Rodriguez & Garcia 2007).

Nanoparticles are nano-scale materials with dimensions less than 100 nm. The small scale size of nanoparticles and its greater surface area per weight are features that significantly promote its potential for application in specific research areas. These include studies in the optical, photonic, electrical, and catalytic domains (Ban et al. 2009). Of late, the application of metal oxide nanoparticles in research related to optoelectronics, field emissions, sensors, photocatalysts, lasers, solar cells and fuel cells have attracted worldwide attention (Hu et al. 2010).

The chemical stability of oxide nanoparticles paves the way for thermal decomposition at high temperature and dissolution in a basic or acidic media (Wang & Hu 2009).

Optical and electronic properties are related to the size of semiconductor nanoparticles (Hoffmann et al. 1995). They are widely applied in areas such as photocatalytic oxidation for environmental remediation, renewable energy technology and DNA determination through the use of chemical and biochemical sensors (Beydoun et al. 1999). By decreasing the size of nanoparticles, the surface area to volume ratio can be increased to significantly influence optical and electronic properties.

Semiconductor excitation resulting from the absorption of light leads to the generation of electrons and hole for charge carriers. The band gap energy of the semiconductor is an important optical property defined as the minimum energy required for charge carriers to move electrons from the valence band to the conduction band. An increase in the band gap leads to an increase in excitation energy of the charge carriers (Coey et al. 2005). Generally, the semiconductor nanoparticles exhibit various crystals and a higher surface to volume ratio. The presence of impurities, interstitial atoms, dislocations, and defects on the surface works as traps to enhance their photo-physical properties (Klingshrin 2007).

As the properties of nano-materials are exclusive in nature many researchers were driven to come up with new and simple techniques to produce cheap nanostructure materials. Research on the electrical and optical properties of zinc oxide began in 1950 (Chen et al. 2006). Zinc oxide nanoparticles (ZnO NPs) have a particularly wide band gap range of 3.37 eV with 60 meV as the excitonic binding energy. These properties render ZnO NPs significant in several applications (Sato & Yoshida 2002). ZnO NPs are used in photocatalysis, sensors and desensitized solar cells because they possess favourable optical, electrical, and chemical properties (Ollis & Al-Elkabi 1993). Commonly used as semiconductors, ZnO NPs can be obtained in the hexagonal wurtzite crystalline structure form. An advantage attributed to ZnO is its large capacity for solar spectrum absorbance. This advantage makes it applicable

under solar light for the degradation of various organic pollutants. Although Hydroxyl Titania (TiO_2) is considered the most efficient photocatalyst, its drawback is the fact that it only responds to ultra violet light (Fabbri et al. 2006).

Photocatalysis is process in which the acceleration rate of a photoreaction occurs in the company of a catalyst. It was discovered in 1972 by Honda and Fujishima via an investigation on the photoelectrolytic process (Legrini et al. 1993). Due to their optical properties, large surface areas, stability and low cost, nanoparticles were deemed the most appropriate nano-scale material for semiconductors.

Photocatalytic reactions occur with the excitation of a semiconductor by the absorption of energy from a photon similar to, or more than the band gap energy. Produced on the surface of the semiconductor, photogenerated electrons (e^-) reduce the electron acceptor and the holes (h^+) oxidize the electron donor. In an aqueous suspension, positive holes (h^+) react with adsorbed water and ^-OH groups to result in strong oxidizing $\cdot OH$ radicals. Additionally, the free electrons (e^-) react with adsorbed molecular O_2 to produce $\cdot O_2^-$ superoxide anions that may also contribute to the production of $\cdot OH$ radicals through the formation of $HO\cdot_2$ radicals and H_2O_2 . It is believed that the reaction of the $\cdot OH$ radicals with organic pollutants is a key reactionary step leading to the degradation of these compounds. From an environmental viewpoint, calls for the harnessing of solar power as an alternative source of energy have increased significantly during the last decade. The application of solar light in some countries has proven to be trouble-free and economically acceptable for the photocatalysis process. Solar light, comprising 43-46% visible and 4-5% ultraviolet light is a free, environmentally friendly, and renewable source of energy (Parent et al 1996). The limited recombination of photo generated electrons and holes are among the effective control factors in the application of photocatalysis using semiconductors (Chen et al. 2007).

Several procedures have been proposed for enhancing the efficiency of semiconductor nanoparticles. These include the (i) addition of chemical oxidants, (ii) doping with other cations and surface modification, (iii) coupling of the photocatalyst

with other photosensitizers and (vi) coupling of the photocatalyst with other types or with AOPs (Gaya et al. 2008). Some studies have reported that the photocatalytic activity of semiconductors is dependent on two main factors: the amount of adsorption of the pollutant on the surface, and separation efficiency of electron-hole pairs (Liu et al. 2008). However, in recent years, doping of the semiconductor has been carried out to enhance adsorption of pollutants and shift absorption to visible light (Herrmann et al. 2007). The use of transition metals as dopants to increase the surface area and reduce the rate of electron-hole pair's recombination was reported in previous research (Vione et al. 2005).

1.2 PROBLEM STATEMENT

For the last two decades, ZnO NP has been considered the more appropriate photocatalyst when compared to TiO₂. The wide band gap (3.37 eV) of ZnO NP makes it capable of absorbing a larger fraction of the solar spectrum than TiO₂. Thus, under direct solar light, ZnO as a photocatalyst is the preferred choice for the photocatalysis process.

Many previous studies have used a capping agent or a surfactant to manage the size of semiconductor nanoparticles (Kim et al. 2006). Capping agents such as thiolphenol (Amma et al. 2006) and mercapto acetate (Wageh et al. 2003) are toxic chemicals and eradicating them from the surface of the synthesized nanoparticles will prove to be an arduous task. Therefore, a large-scale production of nanoparticles would undoubtedly result in serious contamination of the environment. At same time, a surfactant such as polymer (Ethylene glycol, polyethylene glycol, triethanolamine), while improving the surface of nanoparticles during the synthesise process, will add substantially to the cost in a large-scale application of the process.

The starting material molar ratio was adjusted to investigate its ability to manage the size and shape of the products (Dios et al. 2005). Other studies have developed nanoparticles of different sizes by altering the solution pH (Lepkov'a et al. 2007; Alias et al. 2010). The first part of this study involves the effects of starting material molar ratio, the pH of the medium and calcination on the synthesizing of

smaller sized ZnO NPs through the sol gel technique. To optimize these parameters for the production of smaller particle size, design of experiment (DOE) was applied as a statistical technique to create a model of the optimization process. DOE is based on response surface methodology (RSM). It ensures a good relationship between the multiple parameters so that the determination of optimum conditions required for the realization of a specific desired response can be achieved (Box & Draper 1987). However, in business-related fields, the sol gel process is utilized not only for the production of ZnO, but also other metal oxides such as TiO₂, Fe₂O₃, NiO, CuO and Co₃O₄ nanoparticles under similar optimization conditions for all parameters.

The second part of this study investigates the application of ZnO NPs for the degradation process under solar light with chlorophenols (CPs) serving as a toxic organic pollutant example. The Environmental Protection Agency (EPA) has declared chlorophenols toxic to humans. These compounds were introduced into the ecological system through wastewater released from industrial plants. Traditional methods for the eradication of chlorophenols which include biological and chemical treatments are saddled with disadvantages and limitations. The application of solar light for the photocatalysis process in countries with suitable climates has been seen to be trouble-free and economical. Solar light consisting of 4-5% ultraviolet and 43-46% visible light is free, environmentally friendly and a renewable source of energy. The limit of recombination of the photo generated electrons and holes are among the factors determining the photocatalytic efficiency of semiconductors (Gaya et al. 2008). The ZnO properties are improved by the doping of various transition metal ions with different valences such as tri (3⁺) and tetra (4⁺). This leads to the increased presence of electrons in the conduction band selected for this study. These doping ions enhance absorption by shifting from UV range to visible or by increasing the surface area through the reduction of particle size. Other candidates for our study on environmental pollutants include methyl blue, methyl orange methyl red and lignin. Investigations on degradation will be conducted under optimal experimental conditions.

1.3 RESEARCH OBJECTIVES

The overall objective of this study is to determine the effectiveness of a photocatalyst in the degradation of pollutants from water under direct solar light, while the specific objectives of this investigation are:

1. To optimize the process parameters for ZnO NP synthesis by managing the particle size using the RSM design and investigate by characterization.
2. To modify the properties of ZnO NPs by the doping of metal transition ions as the titanium (Ti^{4+}) and iron (Fe^{3+}), rare earth such as (Sm^{3+}) with a concentration of 0.0-1.0 wt. %.
3. To determinate the activity of ZnO NPs for photodegradation of chlorophenols by determining the significant factors using the 2-Level factorial for survey and the RSM design for optimization.
4. To compare the photodegradation efficiency of chlorophenols using ZnO NP and doped ZnO NP and evaluate the toxicity of intermediate compounds before and after degradation through the inhibition zone method using *Escherichia coli* bacteria.
5. To determine the mechanism of chlorophenols degradation using gas chromatography–mass spectrometry (GC-MS).

1.4 SCOPE OF THE STUDY

The Sol gel method was employed for the synthesis of ZnO NPs to determine the optimum conditions for preparation. These include the molar ratio of starting materials, pH and calcination temperatures. The optimum conditions for producing smaller sized ZnO NPs are applied to synthesize other metal oxides so that it would be easy to scale up the process in future. This study sought to improve the optical properties of ZnO NPs by either shifting to them to a visible region or increasing their surface areas for higher photocatalytic activity under solar light. For this purpose, (Fe^{3+}), (Sm^{3+}) and (Ti^{4+}) were used for the doping of metal ions. The degradation of chlorophenols in water by ZnO and doped ZnO NPs under solar light and optimal conditions were then compared. All experiments were conducted with a batch slurry reactor to study the effects of parameters on the photocatalytic degradation of

chlorophenols. Parameters such as loading of the catalyst (0.5 - 2.5 g/l), pH solution (4-8), calcination temperatures (400-600°C), initial concentration (50-150 mg/l) for 2-CP, 2, 4-DCP, 2, 4, 6-TCP and solar intensity (clear day, semi-cloudy day and cloudy day) were used for process optimization. Fig.1.1 shows the flowchart of overall steps of this study from synthesis of ZnO NPs up to application and analysis.

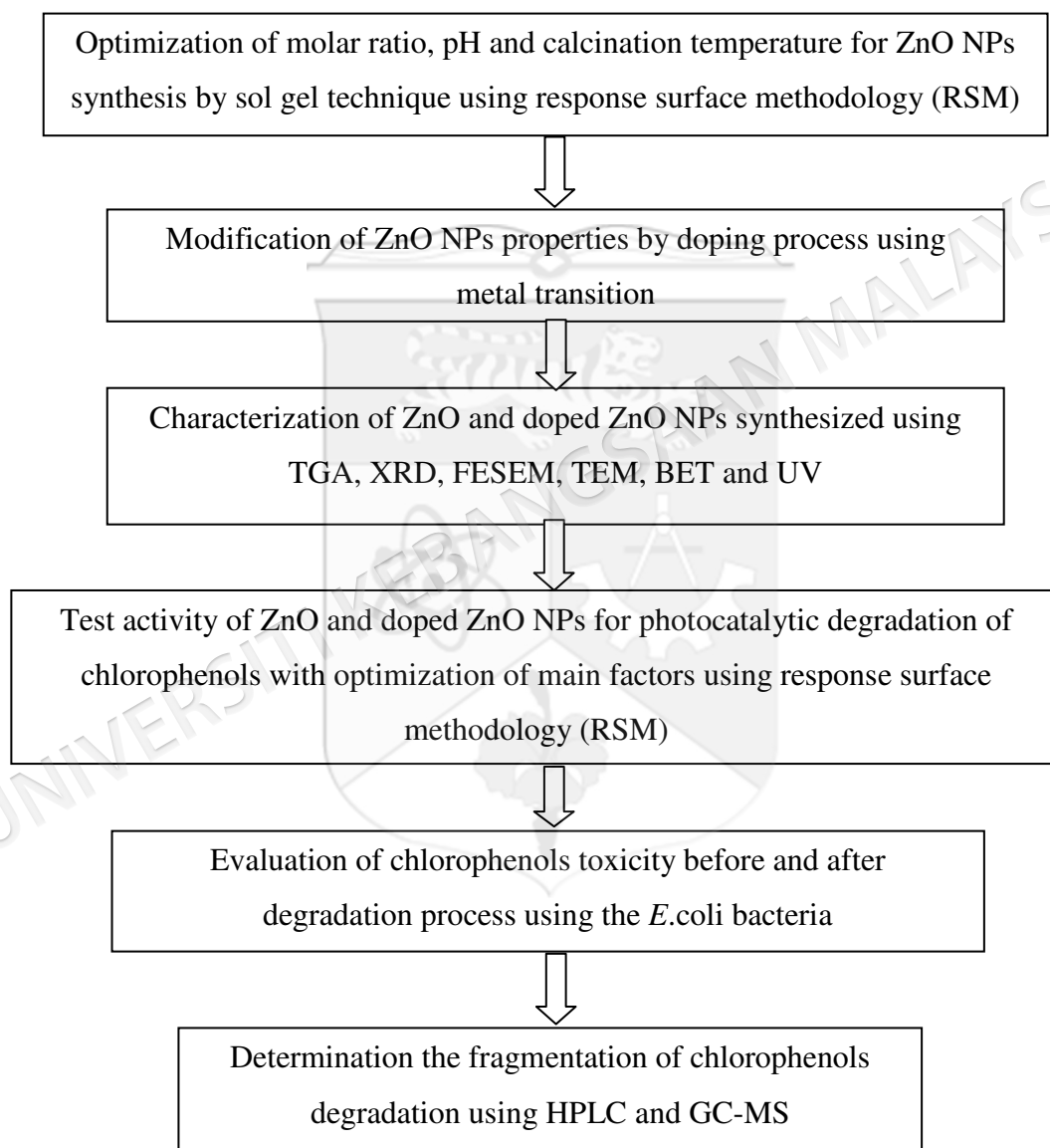


Figure 1.1 Flowchart of overall steps for synthesis and application of ZnO and doped ZnO NPs

Additionally, the kinetic study of chlorophenol degradation by ZnO and doped ZnO NPs under solar light was included in this study. The fragmentation of chlorophenols to low molecular intermediate compounds was achieved through High-performance liquid chromatography (HPLC) combined with Gas chromatography-mass spectroscopy (GC/MS). The toxicity of chlorophenols before and after degradation was evaluated with the use of *E.coli* bacteria. The other colour pollutants were also used to evaluate the activity of synthesized ZnO NPs under solar light.

1.5 THESIS OUTLINE

This research comprises five chapters. The first chapter provides general information on the properties and applications of nanoparticles. Also included are the problem statement, objectives, and scope of this study. Relevant literature on the properties of ZnO NPs as a heterogeneous photocatalyst, types of ZnO NPs, synthesizing methods of ZnO NPs, evaluation of ZnO NP size (OD) by the sol gel method, enhancement of ZnO NP properties through the doping of various ions, and the effects of parameters on the photocatalysis process was reviewed in the second chapter. The third chapter presents a discussion on the methodology of this study and describes the materials and instruments used to achieve the various objectives. The fourth chapter emphasizes on the design of experiment (DOE) and includes an account on the optimization of process parameters for ZnO NPs synthesized by the sol gel method based on the D-optimal design. The fifth chapter focuses on a comparison between ZnO NPs and doped ZnO NPs (both synthesized by the sol gel method) regarding their effectiveness in the removal of chlorophenols from water under direct solar light. The sixth chapter comprises conclusions and suggestions for future work based on the findings of this study.

CHAPTER II

LITERATURE REVIEW

2.1 INTRODUCTION

ZnO is an inorganic compound and is an excellent alternative material of the II–VI semiconductor group. Many properties of ZnO such as its electrical conductivity and optical properties make it a candidate for several applications. ZnO shows good potential for applications such as solar cells, laser diodes, gas sensors and photocatalysis due to its wide band gap (3.37 eV) and its large exciton binding energy (60 meV) (Sheng et al. 2007). The piezoelectric property of ZnO indicates that it can be used for surface acoustic wave and electronic devices in other application (Tian et al. 2004). On the other hand, ZnO films have been applied successfully to enhance the short circuit current of solar cells by a heterojunction with copper indium diselenide (Xu et al. 2004).

ZnO has three crystalline forms: hexagonal wurtzite, cubic zinc blende and the rarely observed cubic rock salt, as shown in Figure 2.1. The common and most stable structure of ZnO is the hexagonal wurtzite under ambient conditions (Wang 2004). However, the zinc blende is stabilized when ZnO is grown as a cubic lattice structure on substrates only. Both of these ZnO forms are geometrically tetrahedral. The rock salt form of ZnO can only be produced at a high pressure of around 10 GPa. ZnO in the form of wurtzite consists of a hexagonal unit cell in which the lattice parameters are $a = b = 0.3296$, and $c = 0.52065$ nm (Wang 2004).

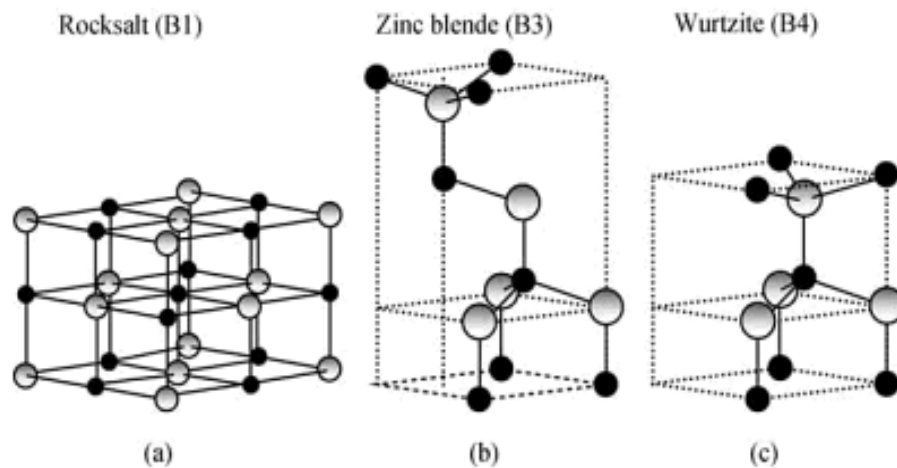


Figure 2.1 Zinc crystal structures (a) cubic rocksalt, (b) cubic zinc blende, (c) hexagonal wurtzite structure.

Source: Morkoc & Özgür 2009

Figure 2.2 shows the wurtzite structure with the positions of the oxygen anions and the Zn cations which produce the tetrahedral unit with a central symmetry. The wurtzite structure of ZnO consists of hexagonal cells with lattice parameters of a , b for the space group of C_{6v}^4 or $P6_3mc$. The structure is indicated as being composed of two hexagonal cells consisting of Zn or O atoms which displace each other on the threefold c -axis. The structure can be explained schematically as layer by layer of planes along the c -axis with coordination of the Zn^{2+} and O^{2-} ions tetrahedrally. Each anion in the wurtzite structure of ZnO is occupied by four cations as a tetrahedral coordination, which shows the sp^3 covalent bonding (Morkoc & Özgür 2009).

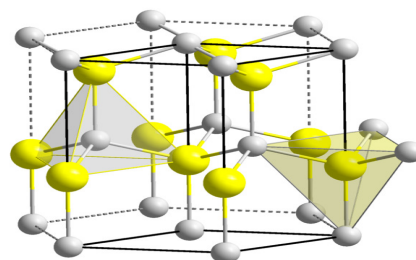


Figure 2.2 Hexagonal wurtzite as stable structure of ZnO form

Source: Morkoc & Özgür 2009

2.2 PROPERTIES OF ZnO NANOPARTICLES

2.2.1 Mechanical Properties

The mechanical properties of all materials include different concepts such as hardness, stiffness and piezoelectric constants, Young's modulus, bulk and yield strength. According to the Mohs scale, ZnO has a hardness of 4.5, thus making it a relatively soft material. Some of the properties of ZnO, such as high conductivity, heat capacity and melting temperature with low thermal expansion, are favourable for ceramics. Among the tetrahedrally-bonded semiconductors, ZnO has the highest piezoelectric tensor, thus making it a good material for piezoelectrical applications which need large electromechanical coupling (Morkoc & Özgür 2009).

2.2.2 Electronic Properties

The large band gap of ZnO (3.37 eV) at room temperature indicates some advantages for breakdown voltages, greater stability under higher electric fields and lower electronic noise. However, it has been reported that the ZnO band gap can be controlled between 3 - 4 eV by alloying it with magnesium oxide (MgO) and cadmium oxide (CdO) (Ozgür et al. 2005). ZnO is a metal oxide semiconductor that exhibits n-type conductivity without doping. The doping of ZnO is easily carried out by the substitution of Zn with group-III elements (transition metals) or by the substitution of oxygen with group-VII elements. On the other hand, the doping by p-type is still difficult because of low solubility and the limitation of the current. The dopant groups of the p-type, such as the group-I (Li, Na, K) and group-V (N, P, As) elements, do not show considerable conduction at room temperature (Ozgür et al. 2005).

2.2.3 Optical Properties

ZnO has good optical properties which have been reported in many previous studies over the last three decades. The wide band gap (3.37 eV), large exciton binding energy (60 meV) and higher reactive recombination are excellent properties for wide applications of ZnO. The exciton energy of ZnO is the main feature in laser

applications for operations based on excitonic transitions as opposed to the electron–hole plasma.

Additionally, the nanoparticles of the semiconductor have two effects on the optical properties either intrinsically or extrinsically. The excitonic effects between the electrons and the holes in the conduction and valence bands respectively are due to the Coulomb interactions called intrinsic optical transitions. The excited state of the free excitons indicates that ZnO has very few low impurities. The creation of electronic states (neutral or charged donors and acceptors) in the band gap by dopants/impurities and complexes which affect optical absorption and the emission process are known as extrinsic properties. The optical properties of ZnO have been the focus of experimental studies using different techniques such as optical absorption, reflection, transmission, photoluminescence, etc.

2.2.4 Magnetic Properties

Diluted magnetic semiconductors (DMS) such as ZnO have good magnetic properties which are considered for spintronic applications. Generally, magnetic materials are classified according to varying degrees of the response range of the magnetic field. Materials are classified into the following four groups according to their magnetic behaviour: diamagnetic, paramagnetic, ferromagnetic, and antiferromagnetic. Diamagnetism is a fundamental property that has been reported for all materials, including ZnO, which have very weak magnetic fields. Diamagnetic materials consist of atoms that have no net magnetic moments, in which all the orbital shells are filled and there are no spinning unpaired electrons. Paramagnetic materials exhibit atoms or ions that have a net magnetic moment because the orbitals are partially filled by unpaired electrons, for example, in transition metals and some rare earth minerals (Morkoc & Özgür 2009). However, in ferromagnetic materials the atomic magnetic moments in a lattice interact to align parallel to each other. Moreover, antiferromagnetic materials are ferromagnetic materials with the points in the opposite direction.

2.2.5 Physical Properties of ZnO

The physical properties of ZnO are listed in Table 2.1 and all the values reported are for the general properties (Wang 2004). These properties of semiconductors are reduced to smaller scale nanometres, and therefore, some of the properties, such as band gap energy (for example), will be changed by quantum size effects. The physical properties are a critical part of the design of devices upon application. For that reason, the testing of the individual properties of ZnO is important for the manufacture of nanoscale devices in the future.

Table 2.1 Physical properties of ZnO

Properties	Value
Molecular formula	ZnO
Molecular Weight	81.4084 g/mol
Appearance	Amorphous white or yellowish white powder
Density	5.607 g/cm ³
Melting Point	1975 °C
Boiling point	2360 °C
Solubility in water	0.16 mg/100 ml
Refractive Index :	2.004
Lattice constants	a=b= 0.32469 ,c=0.52069 nm
Excitation effective energy	60 meV
Specific heat	0.125 cal/gm
Thermal conductivity	0.6W/cm/°C
Heat Capacity	C _p = 9.62 cal/deg/mole at 25°C
Coefficient of Thermal Expansion	= 4 x 10 ⁻⁶ /C
Electron effective mass	0.24
Electron mobility (T = 300 K)	200 cm ² /V s
Hole effective mass	0.59
Hole mobility (T = 300 K)	1 m ² /V s

2.3 SYNTHESIS METHOD OF ZnO NANOPARTICLES

In the last two decades, the synthesis of metal oxide nanostructures and investigations into their characterization has potentially led to the production of specific properties for many nano-file applications. Different processing techniques for the synthesis of the ZnO nanostructure have been explored in the literature, which can be divided into two main categories, (i) the vapour phase growth process and (ii) the solution phase growth process as shown in Figure 2.3.

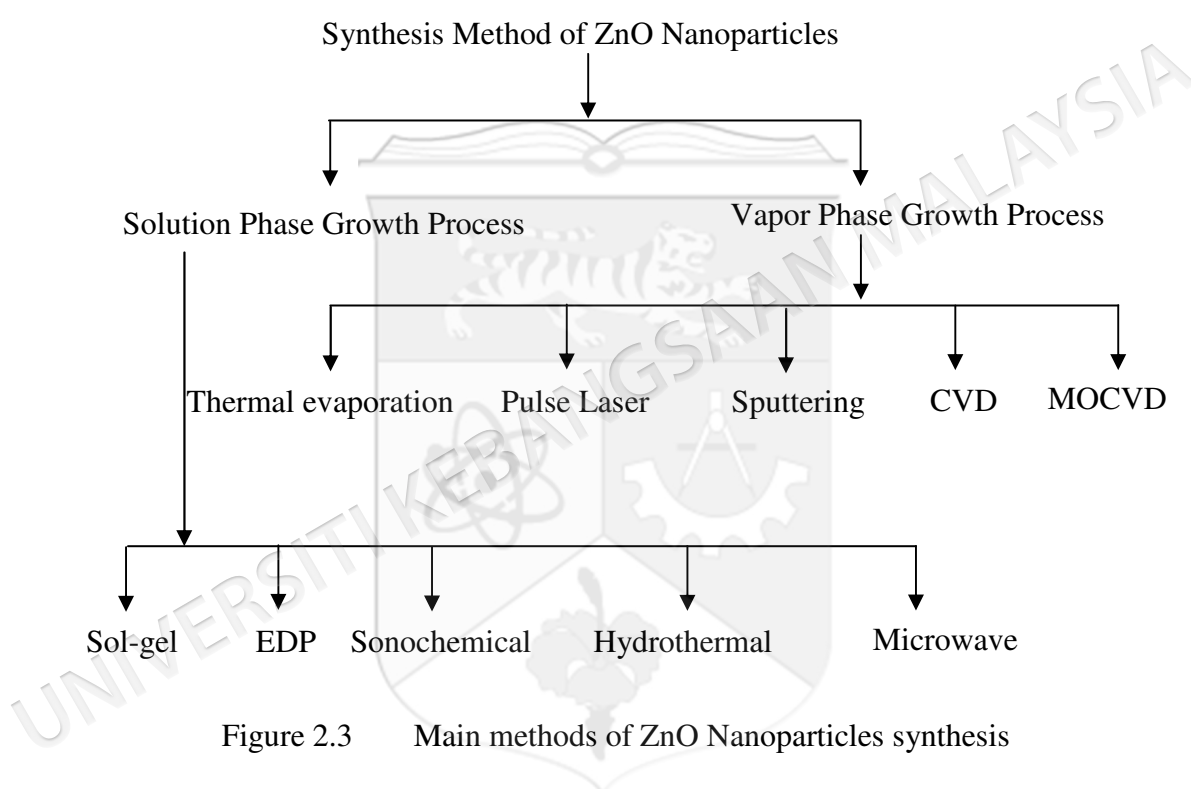


Figure 2.3 Main methods of ZnO Nanoparticles synthesis

2.3.1 Vapor Phase Growth Process

The vapour phase deposition method has been used to produce the different ZnO nanostructures based on the reaction between oxygen gas and metal vapours. At high temperatures, materials form vapours first and then condensation, nucleation and growth occur at relatively lower temperatures. To control the size of the nanostructures, the aspect ratio and crystallinity, together with other techniques have been included, such as thermal evaporation, pulse laser deposition, metal organic chemical vapour deposition, sputtering, thermal chemical vapour deposition, etc.

A. Thermal Evaporation Process

The thermal evaporation method is considered to be the simplest method and is mostly used for the preparation of different types of nanostructures. It consists of a high temperature furnace for vaporizing the material and deposition devices to produce the nanostructures. The vapour of the material is formed by using a physical or chemical method first and that vapour is then condensed under certain conditions (temperature, gas flow and pressure). The morphology of the nanostructure using the thermal evaporation method is not only influenced by temperature, pressure, time and gas flow but also by the source of the initial material and substrate. Many studies have reported on the synthesis of desired nanostructures by controlling the process parameters such as temperature, pressure, time and gas flow (Umar et al. 2006).

B. Pulse Laser Deposition

The Pulse Laser Deposition method (PLD) is proficient for producing the thin films called laser ablations. It is able to make thin films of any materials, which are difficult or impossible to produce by other techniques. The method involves focusing a pulsed laser beam onto the surface of the desired solid material to form a vapour by the absorption of electromagnetic radiation. The vapour of the material is presented as glowing plasma while in front of the target surface and the ablation is carried out in a vacuum. Some of the parameters, such as the laser energy density and the pulse repetition rate, can be controlled within the process. The pulse laser deposition method has been reported to be used for producing ZnO nanostructures (Sun et al. 2011).

C. Sputtering process

The sputtering method is a physical process in which the atoms of a solid material flow as gas due to bombardment by energetic ions. Metallic atoms are produced from a target surface by bombardment using an ionized species to deposit a coating onto the substrate. This method has been widely used for the synthesis of ZnO nanostructures .

D. Chemical Vapor Deposition

Chemical vapour deposition (CVD) is a chemical process for the synthesis of high quality nanostructure films. This process is used widely to fabricate films for optoelectronic device applications and it can easily be used for large-scale production in future. However, another application of the CVD method is to produce high purity of bulk powders as well as composite materials. When CVD is modified accordingly on precursors of materials used on metal-organics the technique is known as metal-organic chemical vapour deposition and when on the hydride of the precursors it is then called hydride CVD or VPE (HVPE) (Ahuja et al. 1998). The ZnO nanostructure deposition produced by the chemical reaction of the precursors using a carrier gas vaporise into the substrate.

E. Metal organic Chemical Vapor Deposition

Metal-Organic Chemical Vapour Deposition (MOCVD) is widely applied to prepared epitaxial films on a wafer substrate by the deposition of atoms and is mostly employed in the semiconductor industry. In MOCVD, the desired atoms bind with organic molecules and are then passed over a hot plate. When heated, the organic molecules will break up and deposit onto the surface of the substrate as layer by layer of atoms. The unwanted or remaining atoms are deposited onto the reactor wall after the process. As has been widely reported in previous studies on the synthesis of the ZnO nanostructure (Lee et al. 2004), this process can be used to produce materials with specific optical and electrical properties by controlling the thickness of the layers.

2.3.2 Solution Phase Growth Process

The solution phase growth process is another process for the synthesis of several nanostructures. The conditions and facilities required for the growth process are low temperatures and simple instruments to reduce the cost of fabrication compared to the vapour phase growth process. The final product is considered to be of high purity due to the removal of impurities using filtration and the washing of the final precipitates that are produced. The focus is on the commercial production of nanostructures by this method in the future because of the lower cost of this process.

A. Sol-gel Method

The sol-gel method is a simple method for the production of a variety of ZnO nanostructures. This process involves the conversion of the sol from a liquid phase to a solid phase as gel. First, a sol of a precursor material (colloidal suspension) is formed. Then after the required reaction time, the gel can be thermally treated to obtain the final product. Several characteristics such as small particle size, higher specific area, and higher activity of the final product and fast production of a large number of samples have been reported as the advantages of this process (Kaur et al. 2006).

B. Electrochemical Deposition Process

The Electrochemical Deposition Process (EDP) is a convenient method for the synthesis of nanostructures. It is considered to be a low cost method because the precursors are dissolved in an aqueous solution. This method produces different ZnO nanostructure shapes, such as nanoneedles and sheets, through the use of zinc nitrate as an electrolytic solution. Nanoneedles are also synthesized by using zinc foil as the electrode with zinc nitrate solution as the electrolyte (Wu et al. 2006).

C. Sonochemical Method

The sonochemical process has been used to synthesize a variety of ZnO nanostructures with unusual properties. The principle of sonochemistry is essentially based on the acoustic cavitation phenomenon, which includes the formation, growth and collapse of bubbles in an aqueous solution. Hotspots are generated within the collapsing bubbles through adiabatic compression, thus causing the bubbles to implode. In this method, the chemical reaction is enhanced and accelerated by the release of energy from ultrasound irradiation. The sonochemical technique reduces the time needed for the growth of the nanostructure (Krishnan et al. 2006).

D. Hydrothermal /Solvothermal Growth Process

The hydrothermal/solvothermal method is a chemical process for the synthesis of

different ZnO nanostructures with a wide range of operating conditions such as temperature in a liquid medium. Other conditions, such as the starting precursor concentrations, pH, time and temperature of the synthesis can be controlled in this process. The first step involves making a solution of a mixture of precursor materials that is soluble under temperature and pressure above a critical point to improve the solubility of the solid and increase the reaction rate. In this process, all the solutions are mixed and put in an autoclave under certain temperature and pressure. The operating conditions for the process are temperatures of between 100-300°C and pressures above 1 atm., with or without capping agents (Ghoshal et al. 2006).

E. Microwave Method

The microwave method is widely used in the synthesis of nanostructures by heating. Among the many advantages of this method are that it is cheap and it has a short reaction time compared to other convenient methods. The synthesis of different metal oxide nanostructures by using a microwave for the rapid heating of a solution of precursors in water as the solvent have been reported (Cushing et al. 2004). This easy, higher scale method comes at no extra cost, and this is also important to the industrial sector. The microwave method has been used for the synthesis of 1D (one-dimensional) semiconductor such as nanorods, nanowires and nanobelts (Panda et al. 2006).

F. Polyol Method

The polyol method has been widely used recently for the synthesis of catalysts in nanostructures such as 0D ZnO nanoparticles (Samah et al. 2011). This method is combined with other techniques, such as the microwave, and hydrothermal and solvothermal methods, to fabricate the nanostructure materials. The polyol used in the process comprises multiple hydroxyl functional groups that can act as the solvent and stabilizer to control particle growth and prevent agglomeration (Yu et al. 2005). The first step in the polyol method involves adding metal salts as the starting material to Ethylene Glycol (EG) and then refluxing it at the required temperature. After a certain time, an alkoxide is formed as a chain-like, glycolate complex. Finally, the glycolate precursor is converted to the metal oxide through calcining at a certain temperature.

2.4 CLASSIFICATION OF ZnO NANOSTRUCTURE

Generally, nanostructure materials have dimensions of less than 100 nm. Further different classifications based on dimensionality, which is significant for applications, were reported firstly in 1995 (Gleiter 2000) and then in 2000 (Skorokhod et al. 2001). These classifications did not include fullerenes, nanotubes, and nanoflowers as zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D) and three-dimensional (3D) structures. Therefore, a modified classification was given by Pokropivny & Skorokhod (2007) which included all the types of structure that were missing before. Figure 2.4 shows the modified dimensionality classification of nanostructure materials.

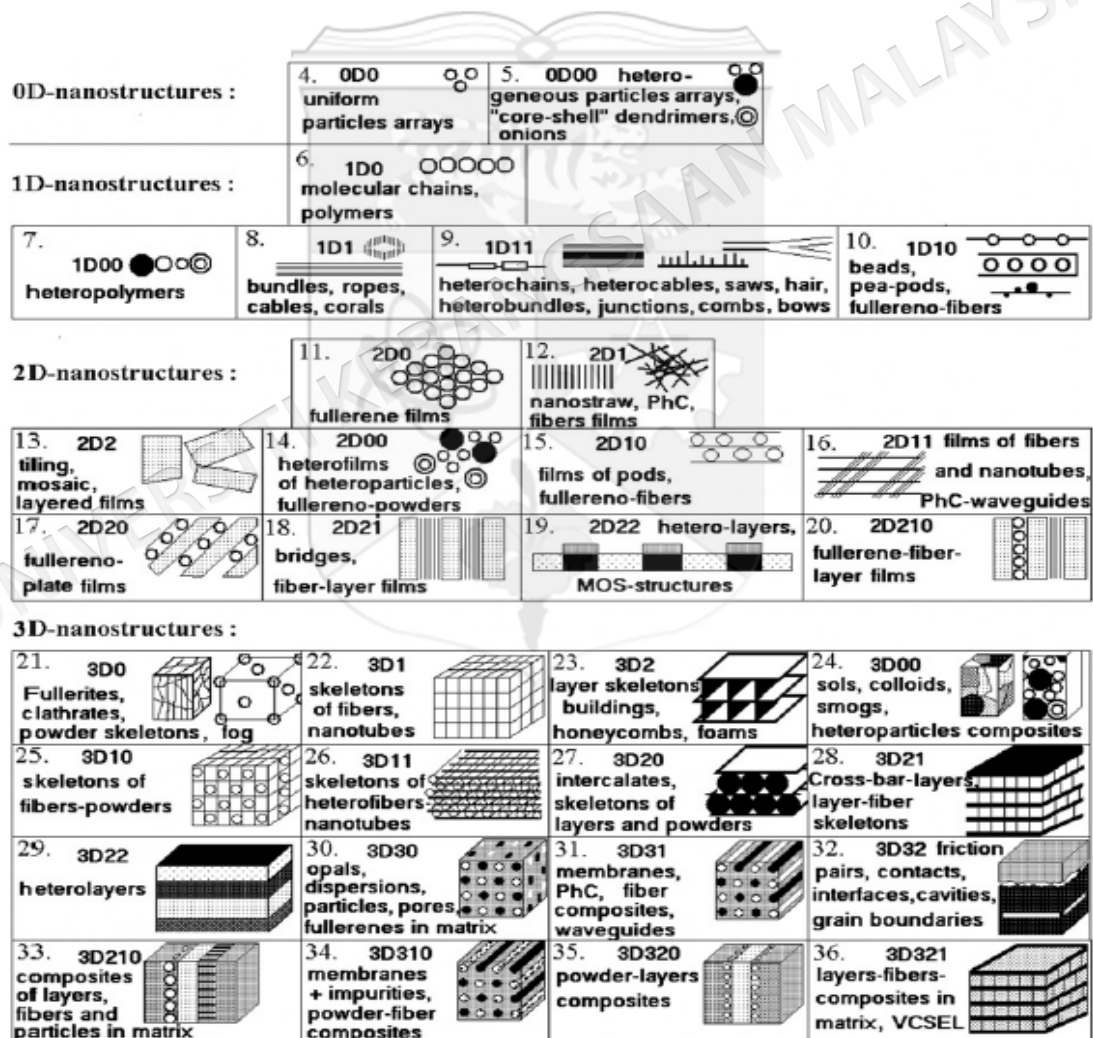


Figure 2.4 Dimensionality classifications of nanostructured materials

Source: Pokropivny & Skorokhod 2007

2.4.1 Zero-Dimensional (0D) of ZnO Nanostructures

The dimensionality of nanostructures plays a main role in the differentiation of nanostructures. Over the last two decades, 0D nanostructured materials with controlled dimensions have been produced by physical and chemical methods. 0D nanostructures of ZnO such as quantum dots (uniform particles), heterogeneous particles, core-shells and hollow spheres have been synthesized using different methods. Some methods synthesized the 0D ZnO nanoparticles in various sizes, such as Chemical deposition (Yang et al. 2003), MVCVD (Eriksson et al. 2009), Pulsed laser ablation (Kim et al. 2011), Sonochemical reduction (Siddiquey et al. 2012), solvothermal (Zak et al. 2011), sol gel (Hassan et al. 2012), Precipitation (Yu et al. 2012), Hydrothermal, (Kumar & Sahare 2012), Polyol method (Chieng & Loo 2012) and CVD (Jin et al. 2007) as shown in Figure 2.5.

2.4.2 One-Dimensional (1D) of ZnO Nanostructures

Over the last decade, 1D ZnO nanostructures, such as nanowires, nanorods, nanotubes and nanobelts, have been used widely in electrochemical, electromechanical, optoelectronic and electronic devices such as field emission devices, piezoelectric nano-generators (Yang et al. 2009), high performance nano-sensors (Wei et al. 2009) and solar cells (Wei et al. 2010). Generally, a new phenomenon is explored to investigate the dimensionality and size of 1D ZnO nanostructures. Several techniques are used to synthesize the 1D ZnO nanostructures such as the wet chemical (Vayssieres et al. 2001), physical vapour deposition (Yao et al. 2002), metal–organic chemical vapour deposition (MOCVD) (Yuan et al. 2004), pulsed laser deposition (Hong et al. 2009), sputtering (Chiou et al. 2003), Thermal evaporation (Kang et al. 2009), CVD (Protasova et al. 2011), Hydrothermal (Zhang et al. 2012), Sol gel (Musat et al. 2012), Microwave (Mahpeykar et al. 2012), Sonochemical (Oha et al. 2009) and (i) Electrochemical deposition (Elias et al. 2008) methods. Figure 2.6 shows the variety of 1D ZnO nanostructures prepared by the different methods.

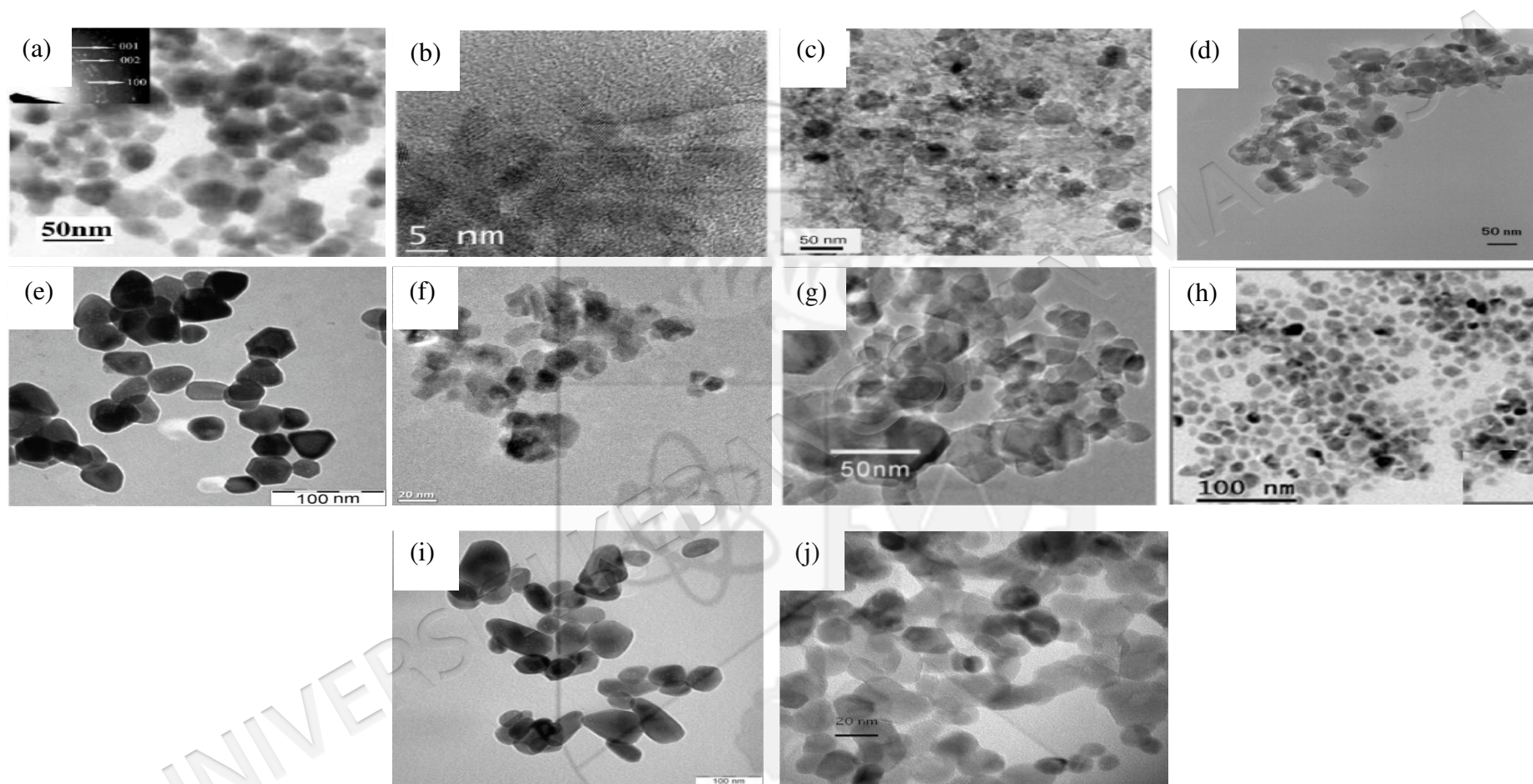


Figure 2.5 The 0 D TEM images of ZnO nanoparticles prepared by several methods as:(a) Chemical deposition, (b) MVCVD, (c) Pulsed laser ablation, (d) Sonochemical reduction, (e) solvothermal, (f) sol gel,(g) Precipitation, (h) Hydrothermal, (i) Polyol method,(j) CVD.

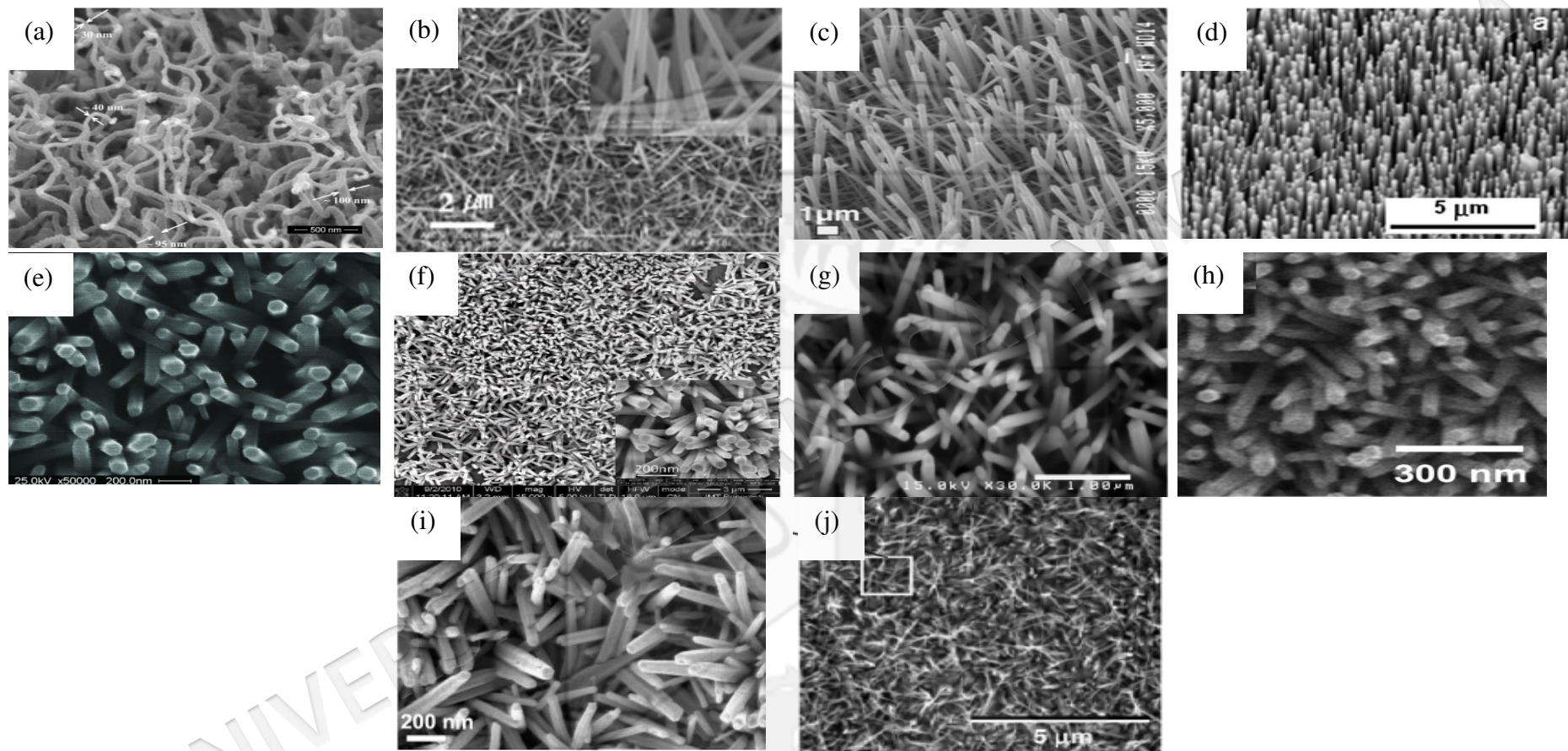


Figure 2.6 The 1 D SEM images of ZnO nanostructures prepared by several methods as: (a) Pulse laser deposition, (b) Thermal evaporation, (c) MOCVD, (d) CVD (e) Hydrothermal, (f) Sol gel, (g) Microwave, (h) Sonochemical, (i) Electrochemical deposition, (j) Sputtering process.

2.4.3 Two-Dimensional (2D) of ZnO Nanostructures

Over the last decade, 2D ZnO nanostructures have been synthesized with different properties for bulk applications. However, recently 2D ZnO nanostructures have been developed with characterizations depending on the shape for specific applications such as nanodevices (Kim et al. 2009). Additionally, 2D ZnO nanostructures are also used as novel materials in other applications such as photocatalysts, sensors, nanoreactors and nanocontainers (Pradhan & Leung 2008).

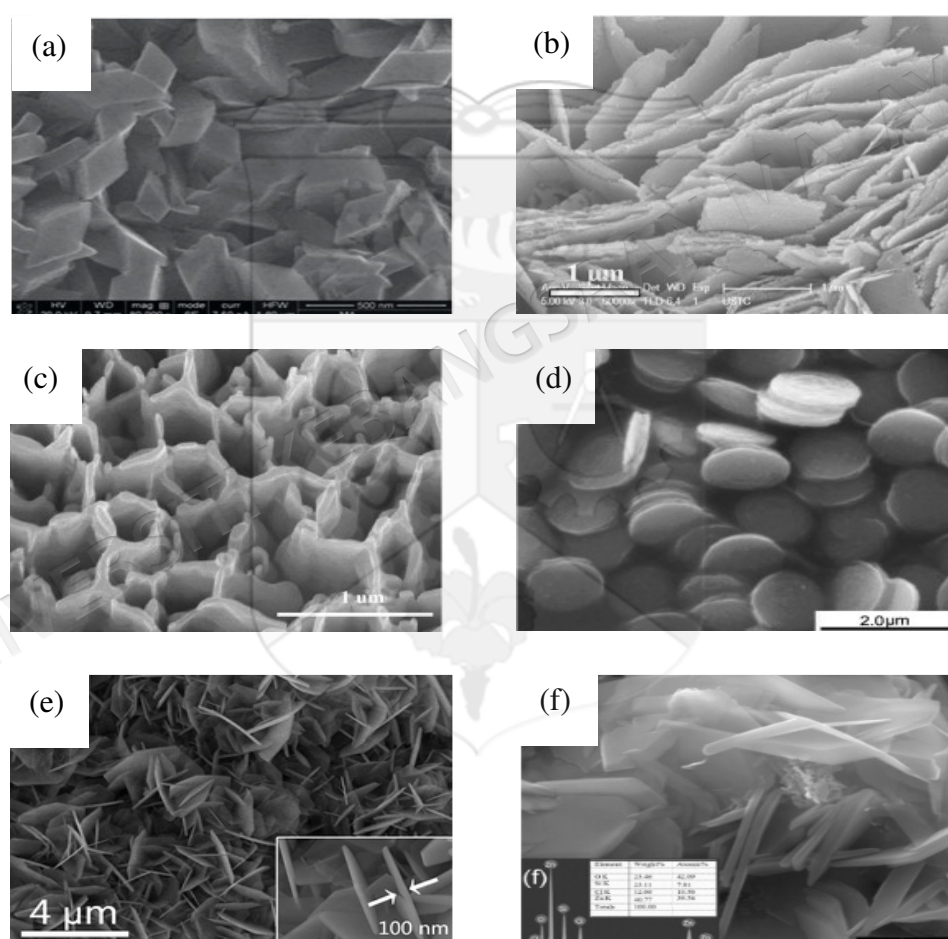


Figure 2.7 The 2 D SEM images of ZnO nanostructures prepared by several methods as:(a) Nanosheet by Electrochemical,(b) Nanosheet by Sol gel,(c) Nanowall by Thermal evaporation,(d) Nanodisks by Hydrothermal,(e) Nanoplates by Hydrothermal,(f) Nanoflakes by Physical vapor deposition.

Different 2D ZnO nanostructures such as nanoplates, nanosheets, nanowalls, and nanodisks are produced by several methods such as electrochemical (Diaz Cano et al. 2013), sol gel (Zhang et al. 2012), thermal evaporation (Yin et al. 2007), hydrothermal (Zeng et al. 2009; Liu et al. 2011) and physical vapor deposition (Yousefi & Sheini 2012) as shown in Figure 2.7

2.4.4 Three-Dimensional (3D) of ZnO Nanostructures

Over the past decade, many researchers have been focused on interesting applications for 3D ZnO nanostructures. The 3D ZnO nanostructures have a large surface area compared to bulk, depending on their morphology such as shape and size. These properties influence the performance of the nanostructures in photocatalysis, magnets and electrodes. Different 3D shape of ZnO nanostructures such as nanoflowers (Ansaria et al. 2009; Lu et al. 2011; Mir et al. 2012), nanotube (Kong et al. 2009), nanocone (Xie et al. 2012; Fu et al. 2007), nanopillars (Behrends et al. 2009) and nanoballs (Uthirakumar et al. 2006) are synthesized by several methods as shown in Figure 2.8.

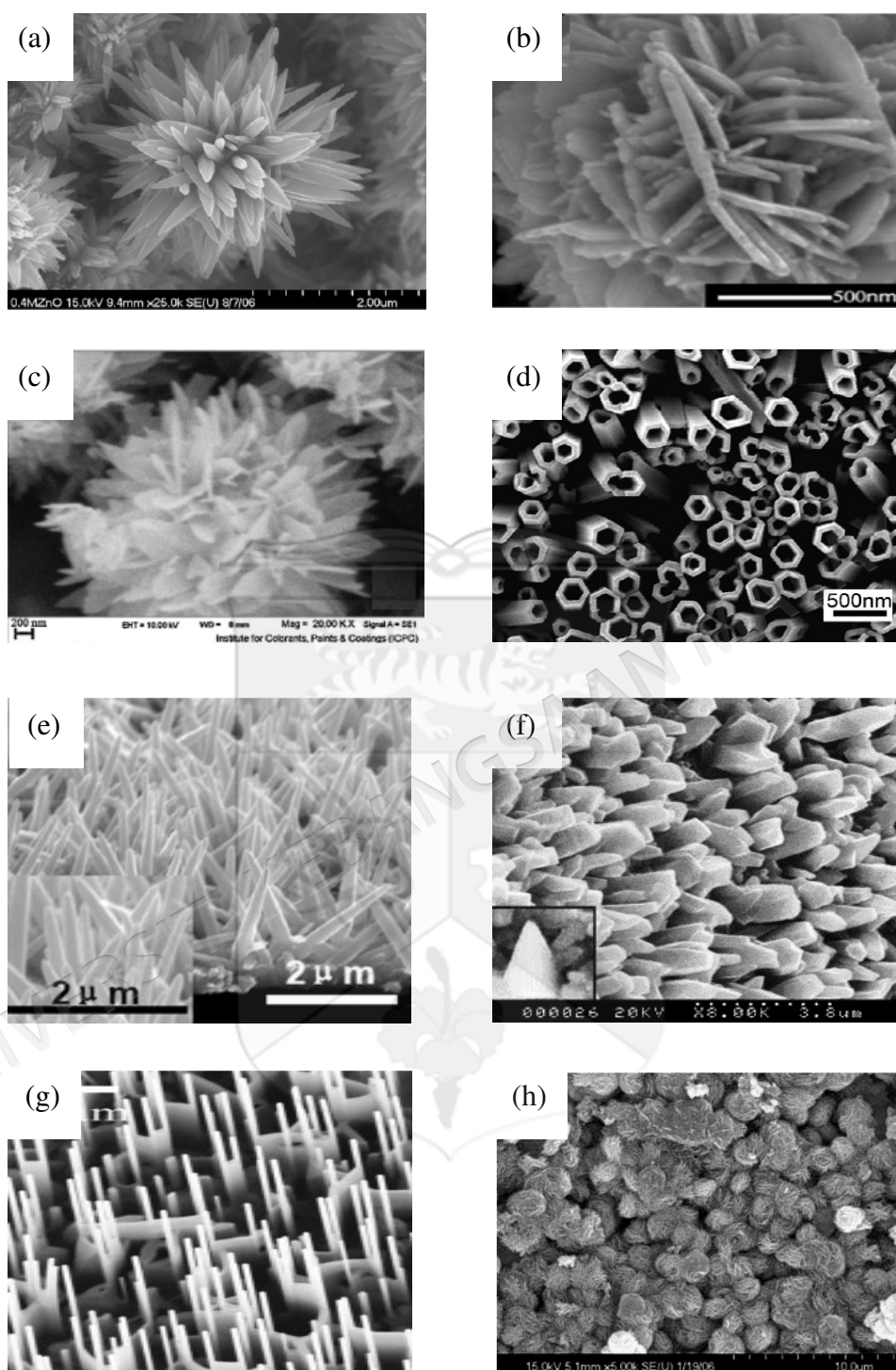


Figure 2.8 The 3D SEM images of ZnO nanoparticles prepared by several methods as (a) & (b) nanoflowers by sol gel, (c) nanoflowers by microwave, (d) nanotube by electrochemical, (e) nanocone by hydrothermal, (f) nanocone by CVD, (g) nanopillars by MOCVD, (h) nanoballs by sol gel.

2.5 SYNTHESIS AND ADVANTAGES OF 0D ZnO NANOSTRUCTURES

The materials on nanoscale dimensions have different physical properties compared to the same materials in bulk form. These properties, such as their activity and selectivity as catalysts and their electronic properties, affect their applications. The 0D ZnO nanostructure is a good material for most applications in specific technologies. Two main properties have been shown to be very important for nanoscale material applications.

2.5.1 Heightened Surface to Volume Ratio and Catalysis

A higher surface to volume ratio is considered to be a property of 0D nano-materials for most industrial applications. It can be defined as the number of surface atoms divided by the total volume of the atoms. Almost all heterogeneous catalyst applications are dependent on this property, which enhances the rate of reaction at the surface of the catalyst. Figure 2.9 shows the principle of the surface to volume ratio, where reducing the size of a cube by five causes an increase in the surface to volume ratio of the same material. In many applications, the nanoparticles connected with nonporous materials, such as zeolite, are applied and these are called hybrid nano-materials.

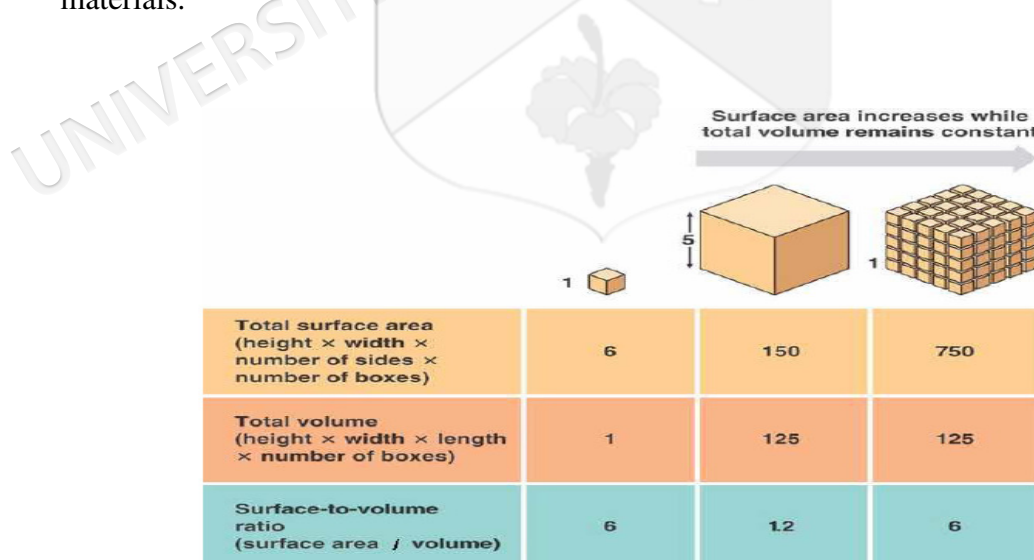


Figure 2.9 Principle of surface to volume ratio

Source: Morkoc & Özgür 2009

2.5.2 Quantum Size Effects

The properties of 0D nanomaterials, such as their optical, luminescent and electrical properties, have been shown to change when the size become smaller. The quantum size effect of semiconductor nanoparticles is relatively larger because of different positions of the Fermi level (Alivisatos 1996). Generally, the Fermi level of a semiconductor lies in between the two bands of valence and conduction, which affects the larger particles on the band gap energy range (change of optical) because these are controlled by the edges of these bands. Another term, blue-shift, is used to describe the quantum-sized effect of a semiconductor in absorption spectra when the size of the particle decreases.

Semiconductors have a wide spacing between energy levels (wide band gap). A decrease in particle size will lead to greater absorption due to a shift to a lower wavelength (higher energy). This shifting is known as blue-shift. The quantum size effect is clearer in much smaller metallic nanoparticles, where the optical properties are directly changed by the band structure. The heightened surface of the metallic nanoparticles leads to absorption of light at a certain range of particle sizes due to interaction between the coherent oscillations and the electromagnetic medium, resulting in the emission of light. This is the case with surface plasmons, which do not occur in bulk materials, and it can be classified as a small size effect that can be measured by electron energy loss spectroscopy in a transmission electron microscope (Bosman et al. 2007).

2.5.3 Synthesis of 0D of ZnO Nanoparticles Using Sol-Gel Technique

The sol-gel method is a wet-chemical technique and is a simple way of preparing metal oxides on a nanometer scale while controlling their properties (Carreon & Gulians 2005). The sol of a solid particle consists of a colloidal suspension in a liquid, which are attached to each other as a network to form the gel. Two different final materials are produced by drying the gel using evaporation or at supercritical conditions. Drying of the gel by evaporation under ambient pressure leads to an increase in capillary pressure, which then results in the shrinkage of the gel network to form a xerogel as shown in Figure 2.10. Additionally, by drying at supercritical

conditions, there will be no capillary pressure in the interface between the liquid and the vapour and little shrinkage will occur, leading to the production of a material known as an aerogel (Sanchez et al. 2005).

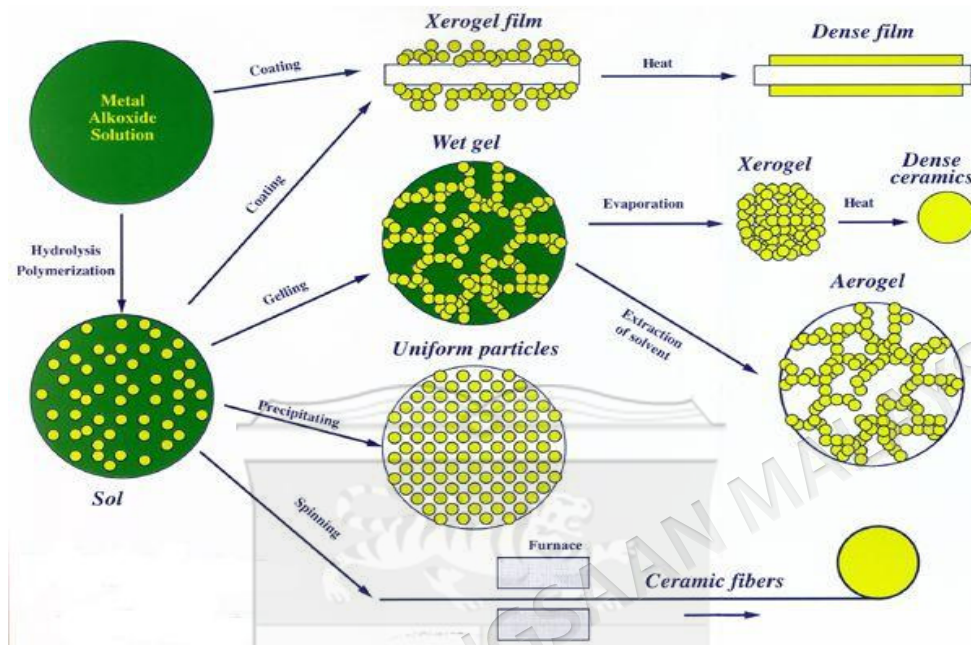


Figure 2.10 Procedures of sol gel process to synthesized of nanoparticles

Source: Brinker & Scherer 1990

In 1846, Ebelmen and Kistler formed a metal alkoxide through the synthesis of a gel, and they were the first to prepare an aerogel in 1932 by drying under supercritical conditions. All materials synthesized by the sol-gel method have many applications such as thin film coatings, catalysts, electrochemical devices, ceramic devices and electrical insulation devices due to their remarkable chemical properties and morphologies (Brinker & Scherer 1990). The general procedure for the sol-gel method involves the preparation of the metal alkoxide by hydrolysis in the presence of a solvent (water or alcohol), followed by the condensation to macromolecules by the formation of sol and finally, the formation of the 3D network to get the gel. Figure 2.11 shows all the steps for the preparation of the metal oxide with a nanostructure by the sol-gel route.

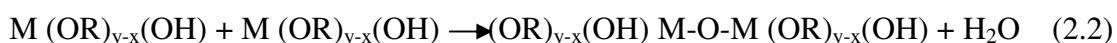
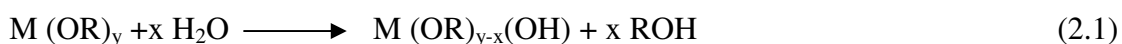
2.5.4 Effecting Parameters on Sol-Gel Preparation

The preparation of a nanomaterial by the sol gel method will affect some parameters in the final properties of the product. These parameters include the gel formation, aging of the gel, solvent removal and heat treatment. The control of the final product can be manipulated through each of these parameters to give the desired product properties.

A. Formation of Gel

A very important step in the formation of the final gel is the dissolution of the metal salt or alkoxide in a suitable solvent (Mehrotra 1992). This can be explained in sol-gel chemistry by the two main reactions, hydrolysis and condensation, on the metal alkoxides and their relative rates which produce the three-dimensional gel network. A hydrolysis reaction is the first step in the production of a hydroxide of precursors in the presence of an alcohol solution. The second step is the condensation reaction, which releases the water from the hydroxide molecules and then connects the molecules to each other to produce a network of metal oxides.

The formation of a gel by the polymerization of metal hydroxide molecules is achieved as the last step in the condensation reaction. The drying of the hydroxide gel to remove the solvent by heat treatment is the final step which affects the properties of the final product. The hydrolysis mechanism involves the reaction between the water and metal alkoxides ($M(OR)_y$), where there is an attraction between the HO^- and the metal centre (M^+). The condensation process takes place when the hydroxide molecules bind together to form the gel and the water molecules are removed as below:



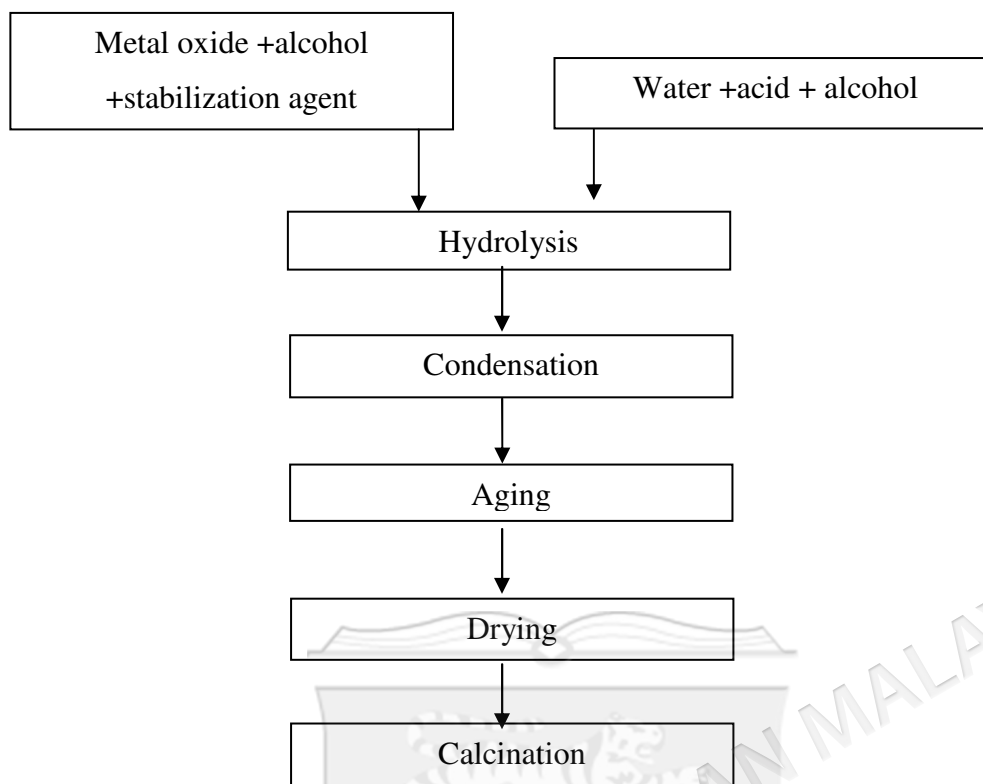


Figure 2.11 Flow chart of gel-sol route to prepare the metal oxide

Source: Brinker & Scherer 1990

The rates of hydrolysis and condensation are essential steps in the control of the final properties of the product, which are affected by the solvent, the alkoxy group, the electronegativity of the atoms and the structure of the metal alkoxide. The hydrolysis and condensation reactions are too fast for the precursors of transition metal oxides, which affect the morphological control of the final product of the oxide. The higher the electronegativity of the metal, the slower is the hydrolysis rate, and vice versa. For example, $\text{Ti}(\text{OEt})_4$ has a hydrolysis rate that is about five times greater than that of $\text{Si}(\text{OEt})_4$, and the gelation time of titanium is faster (in seconds or minutes) compared to silicon alkoxides, which may take days (Janackovic et al. 1998).

Also, the different reactions of metal alkoxides toward water lead to uncontrolled composition and homogeneity of the final product using the sol-gel method. The influence of the OR group size of the metal alkoxide on hydrolysis is related to the reactivity, where a smaller OR group leads to higher reactivity compared to a bigger size. To decrease the reactivity of metal precursors, some additive like

carboxylic acid or functional alcohol is used to modify the reactivity by acting as chelating ligands. Acids and base catalysts have been used to enhance the hydrolysis rate of alkoxides. A catalyst is used for the negative alkoxides to provide a better leaving group and base to provide better nucleophiles (OH^-) for the hydrolysis process. In the case of highly reactive alkoxides, non-aqueous solvents may need to be used to control the hydrolysis in the absence of water rather than by using acids or base catalysts in aqueous solvents (Diao et al. 2001). However, the final properties of ZnO nanoparticles are strongly influenced by the pH solution, temperature of the reaction, and molar ratio of the reactants and additives with the sol-gel method (Sekiguchi et al. 2000).

B. Effects of pH Solution

Critical parameters affect the properties and quality of ZnO such as the size of the particles, the phase formation and the morphology synthesized by the sol-gel process (Alias et al. 2010). It has been reported that the morphology of the ZnO nanoparticles synthesized by the sol-gel method is strongly influenced by the changing pH according to the amount of H^+ or OH^- ions in the sol that effectively determine the polymerization of the Zn-oxygen bonds (Wahab et al. 2009). Moreover, variations of the pH solution also affect the rate of the hydrolysis and condensation reactions, which may lead to changes in the morphology of ZnO. The strength of the surface charge is determined by the pH of the solution, where a higher repulsion of charged particles reduces the probability of the agglomeration of particles, and thus the result will be the formation of a more stable sol or gel in an acidic or alkaline solution. Generally, increasing the growth rate of the process leads to the production of smaller sized particles. A higher surface charge within the growth will lead to repulsions between the particles due to electrostatic charges (increases in H^+ or OH^-). Therefore, these results show that decreasing the growth rate will lead to increased aggregation (Isley & Penn 2008).

C. Aging

After the gel formation, the solvent needs to be removed by a drying process. The time taken for this is known as aging. As long as the pore liquid remains in the matrix,

the gel is not static and can undergo many transformations (Brinker & Scherer 1990; Singh et al. 2012). However, extensive condensation of the alkoxide gel beyond the gel point causes the gel to shrink and the solvent to move out of the pores. Thus, coarsening occurs. This coarsening is a physical process that is related to surfaces that have different radii, which is the result of increasing the average pore size of the gel and decreasing its specific surface area. Some parameters, such as the pH, temperature and time have been reported to have an effect on the aging process, thus resulting in changes to the characteristics of the final gel (Li et al. 2010).

D. Drying

Capillary pressure is a term that is related to the liquid-vapour interface within the evaporation of liquid from a gel network. Small pores have large capillary pressure, and the collapse of pore structures is attributed to the different pressures across pores with different pore sizes. It has been reported that the evaporation rate can be controlled by minimizing the capillary pressure with additives such as glycerol and formamide. On the other hand, the solvent used (ethanol or water) for the preparation has an effect on the surface tensions of the gel network as a result of the different pore volume and surface area of the final xerogel (Gröhn et al. 2011). However, comparisons between xerogels to aerogels by supercritical drying have indicated that the xerogels have attractive properties such as lower densities and higher surface areas. Moreover, another way to remove the solvent from a gel network under moderate conditions is by supercritical drying (Schimmoeller et al. 2011). The advantages of supercritical drying are that it can produce and protect the aerogel with an amorphous structure as a final product for many applications. Therefore, aerogel materials with specific properties such as lower density, higher surface area and higher stability have been prepared using the supercritical drying process (Buesser & Pratsinis 2010).

E. Calcination/Sintering

After the drying process to remove the solvent, additional heat treatment is required to produce the final oxide (catalyst) from a xerogel or aerogel. To complete the heat treatment in the presence of air, flowing oxygen is used to oxidize all the organic

compounds into oxides with different crystallized structural forms. The final properties of the oxides depend on different parameters such as range of temperature, heating rate, time of treatment, and the gases used. The disadvantages of a longer exposure to higher temperatures are that it results in the sintering of particles and leads to a decrease in the surface area of the sample. All the parameters that affect the sol-gel process are summarized in Table 2.2.

Table 2.2 Summary of affect various parameters on sol gel process

step	Target	Affect of parameters
Gel formation	To get a gel	Raw material, solvent type, pH, material concentration ,temperature
Aging	Control of gel properties	Time, temperature, pH
Drying	Solvent removal	Time, drying method(evaporative, supercritical), heating rate
Calcination	Crystallization of final product	heating rate, time, gaseous used

For the past ten years, ZnO nanoparticles are intensively synthesized by the sol-gel method using zinc acetate and zinc nitrate as the precursor materials. The experimental conditions for the perpetration of ZnO nanoparticles such as the type of solvent, the starting material, additive chemicals (capping agent or surfactant), pH of media and concentration of materials have been shown to have a higher influence on the morphology, particle size and properties of the nanoparticles (Masuda et al. 2007). The ZnO nanoparticles with a spherical shape (0D) that have been synthesized by the sol-gel method under different conditions of preparation are given in Table 2.3. However, the type of precursors materials, type of solvent, type of capping agents, type of surfactant have been reported as main effecting factors on size of ZnO nanoparticles.

Table 2.3 Spherical ZnO nanoparticles (0D) synthesized by sol gel method with different conditions.

Precursors	Solvent	Capping agent or surfactant	Additive	Size of particle (nm)	Reference
Zinc acetate dehydrate	Water	-	NaOH	28-39	Singh et al. 2012
Zinc acetate dehydrate	Methanol	p-Xylene	p-Xylene	19	Uthirakumar et al. 2009
Zinc acetate dehydrate	Water	-	Urea	30	Wahab et al. 2008
Zinc acetate dehydrate	Methanol	-	NaOH	36 -49	Alias et al. 2010
Zinc acetate dehydrate	Water	Poly di-ethylene glycol, ethylene glycol	NaOH	20–40	Dakhlaoui et al. 2009
Zinc acetate dehydrate	Water	Poly-vinyl pyrrolidone, di-ethylene glycol	-	34	Jeong et al. 2008
Zinc acetate dehydrate	Methanol	-	Aniline	30	Wahab et al. 2011(a)
Zinc acetate dehydrate	Water	Ethylene glycol	Citric acid	20	Hassan et al. 2012
Zinc acetate dehydrate	Ammonia water	-	Folic acid	23-25	Dutta1& Ganguly 2012
Zinc acetate dehydrate	Ethanol	Triethanola-mine(TEA)	KOH	30	Singh et al. 2009
Zinc acetate dehydrate	Methanol	-	NaOH	24-30	Singh et al. 2011

Continue...

...Continued

Zinc acetate dehydrate	Water	Ethylene diamine tetra acetic acid, Triethanol amine and Tetraethyl ammonium Bromide	NaOH	25-30	Chandrasekaran et al. 2012
Zinc acetate dehydrate	Methanol	Hydroxyl-footed methylneso-rcinarene	-	28 -43	Hammad et al. 2009
Zinc acetate dehydrate	2-propyl alcohol, Water	ethylene glycol	-	>20	Azam et al. 2010
Zinc acetate dehydrate	Methanol	Octadecylamine	NaOH	28	Wahab et al. 2011(b)
Zinc acetate dehydrate	Water		Citric acid, nitric acid	28	Kitture et al. 2011
Zinc acetate dehydrate	Ethanol	Hydroxypropylcellulose	Lithium hydroxide	30	Kim et al. 2007
Zinc nitrate hexahydrate	PVA	PVA	-	25-49	Kundu et al. 2011
Zinc nitrate hexahydrate	Water	Polyethylene glycol , ethylene glycol	-	25	Zhang et al. 2009
Zinc nitrate hexahydrate	Water	Poly(vinyl alcohol)	-	25	Fernandes et al. 2009

Continue...

...Continued

Zinc nitrate hexahydrate	Water	Poly(vinyl alcohol)	-	58	Babu et al. 2013
Zinc nitrate hexahydrate	Water	-	Citric acid	29	Liu et al. 2009
Zinc nitrate hexahydrate	Water	Starch	-	28	Zak et al. 2013
Zinc nitrate hexahydrate	PVA	Poly(vinyl alcohol)	-	25	Hayat et al. 2011
Zinc nitrate hexahydrate	Ethanol	-	Oxalic acid	>28	Shifu et al. 2009
Zinc nitrate hexahydrate	Water	Ethylene glycol	-	>30	Aljawfi et al. 2013
Zinc nitrate hexahydrate	Water	Ethylene glycol	Citric acid	50	Xu et al. 2009
Zinc chloride	Water	Ethylene glycol	citric acid	55	Arshad et al. 2011
Zinc hydroxide	Water	Glycine	Nitric acid	30	Lee et al. 2009

2.5.5 Doping of 0D ZnO Nanoparticles and Their Proprieties

The doping process has played an important role in the development of the ZnO nanostructure fabrication over the last two decades. The main advantage of doping is that it improves the chemical and physical properties of the ZnO nanostructure by controlling and changing these properties, making them desirable for solving problems in applications (Baek et al. 2007). Two types of doping are used for the ZnO nanostructure, the n-type and the p-type, which provide extra electrons or holes in the conduction and valence bands. The dopant atoms (impurity atoms) act as donors or acceptors of the intrinsic ZnO nanostructure. The donor dopant atoms have more electrons than the host atoms, which can be replaced in the intrinsic ZnO lattice. The ionization of ZnO by photon energy indicates that the extra donor electrons have moved to the conduction band. In the n-type of doping, more electrons (negative charge, n) are added to the conduction band, thus increasing the carrier concentration of ZnO. In the n-type doping of the ZnO nanostructure, the Fermi energy level is higher than that of the intrinsic ZnO nanostructure, which is close to the conduction band as shown in Figure 2.12(a). On the other hand, the p-type of doping has a lower Fermi energy level than the intrinsic ZnO nanostructure, which is close to the valence band. The acceptor of the dopant atom has lower electrons than the host atoms that they replace in the intrinsic ZnO nanostructure. The accepted electrons from the valence band of ZnO create excessive holes (positive charge, p) in the intrinsic ZnO nanostructure as shown in Figure 2.12(b). Generally, the dopant of the ZnO nanostructure leads to changes in behaviour and phenomena for applications compared with the bulk ZnO.

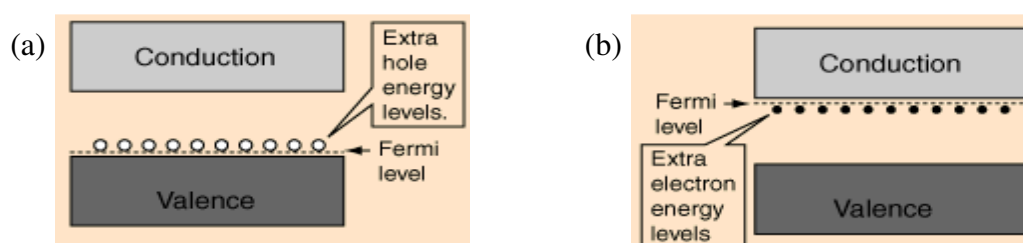


Figure 2.12 Types of ZnO nanostructure doping, (a) n-type, (b) p-type

Source: Morkoc & Özgür 2009

One advantage of ZnO is its large absorbance of the solar spectrum compared to other semiconductors such as TiO₂, making ZnO suitable for applications under solar light (Behnajady et al. 2006). In countries that have sufficient quantities of solar light, the use of it for photocatalysis is easy and economically acceptable. Solar light, consisting of 43-46 % visible and 4-5 % ultraviolet light, is a free, environmentally friendly and renewable source of energy (Sakthivel et al. 2003). The recombination limit of the photo-generated electrons and holes is one of the control factors for the photocatalytic efficiency of semiconductors. Improvements in the properties of semiconductors using dopants have been reported in earlier years (Chen et al. 2007). Additionally, to reduce the rate of the electron-hole pair recombination, doping with transition metals such as Fe³⁺ and Ni²⁺, Co²⁺ and Cu²⁺ are used in ZnO nanoparticles to improve their optical properties and morphology.

However, if these enhancements can be accomplished, ZnO nanoparticles would offer an attractive option for environmental applications due to their efficient use of sunlight as the source of energy. Doping with various concentrations of dopants not only enhances the electron-hole pair separation by decreasing the band gap to take advantage of the shifting of the absorption to the visible light spectrum but also decreases the size to get a higher surface area (Baek et al. 2007; Debernardi & Fanciulli 2007). Metal-oxide nanoparticle semiconductors that are doped with trivalent rare earth ions make good optical materials. These materials have wide applications in different fields, such as in biosensors, optical communications and photocatalysis (Sheng et al. 2007; Xiao et al. 2008). Lanthanide ions enhance the optical absorption of photocatalysts at longer wavelengths and increase their activity under visible light (El-Bahy et al. 2009). A semiconductor doped with Sm³⁺ ions becomes good material for photocatalysis (Hu et al. 2007) and it has been compared with other lanthanides (Chen et al. 2007). A comparison of different dopants on ZnO nanoparticles prepared by the sol-gel method with their conditions and properties are summarized in Table 2.4. However, indicates the affecting of dopants on the optical properties and particle size of ZnO nanoparticles.

Table 2.4 Different doping of ZnO 0D nanoparticles (spherical) synthesis by sol gel method and their properties

Metal doping with source	Band gap (eV)	% of doping	Particle size (nm)	Properties	Capping, surfactant	Reference
Ni ²⁺ , Ni(NO ₃) ₂	3.15	0.5 wt.	21	visible		Kant & Kumar 2012
Ni ²⁺ , Ni(NO ₃) ₂	-	0.05 wt.	25	visible		Pathak & Purohit 2013
Ni ²⁺ , Ni(NO ₃) ₂	2.6	1 mole	18	visible		Shifu et al. 2009
Mn ²⁺ , Mn(NO ₃) ₂	-	6 at.	30	-		Asmatulu et al. 2010
Mn ²⁺ , Mn(CH ₃ COO) ₂	2.2	1.0 wt.	15-35	-		Abdollahi et al. 2011
Mn ²⁺ , Mn(CH ₃ COO) ₂	3.12	0.1 wt.	40	-	Diethanol-amine	Abrishami et al. 2012
Mn ²⁺ , Mn(NO ₃) ₂	-	6 at.	30 nm	-	ethylene glycol	Asmatulu et al. 2010
Co ²⁺ , Co(CH ₃ COO) ₂	-	0.05 wt.	24.4	visible	hydrazine hydrate	Xu et al. 2009
Co ²⁺ , CoCl ₂	3.30	5 wt.	20	-	ethylene glycol	Arshad et al. 2011
Zr ⁴⁺ , Zr(NO ₃) ₄	-	0.05 wt.	60	-	ethylene glycol	Zhang et al. 2011
Eu ³⁺ , Eu ₂ O ₃	-	4 at.	22	-	ethylene glycol	Singh et al. 2008
Cu ²⁺ , Cu(NO ₃) ₂	-	3 wt.	40	-	-	Liu et al. 2010
Al ³⁺ , (Al(NO ₃) ₃) ₃	3.21	5 at.	34-40	-	ethylene glycol	Chen et al. 2008
Fe ³⁺ , FeCl ₃	2.75	20 wt.	19	visible	mono-ethanolamine	Aydın et al. 2013

Continue...

...Continued

Fe^{3+} , $\text{Fe}(\text{NO}_3)_3$	-	5 mole	12.41	visible	ethylene glycol	Hassan et al. 2012
		10 mole	10.58	-		
Fe^{3+} , $\text{Fe}(\text{SO}_4) \cdot 7\text{H}_2\text{O}$	-	5 at. %	15 -35	visible	sodium dodecyl sulphate	Mishra & Das 2010
Ag^{2+} , AgNO_2	-	2 at.	20.9	visible		Wang et al. 2004
Cr^{3+} , $\text{Cr}(\text{NO}_3)_3$	-	3 at.	11	visible		Liu et al. 2009
Sm^{3+} , $\text{Sm}(\text{CH}_3\text{CO}_2)_3$	3.21	1 at.	14	visible		Liu et al. 2010(a)
Dy^{3+} , $\text{Dy}(\text{CH}_3\text{CO}_2)_3$	3.27	1 at.	12	visible		Liu et al. 2010(a)
Nd^{3+} , $\text{Nd}(\text{CH}_3\text{CO}_2)_3$	3.30	1.25 at.	14	visible		Liu et al. 2009
Tm^{3+} , $\text{Tm}(\text{CH}_3\text{CO}_2)_3$	3.27	0.45 at.	15	visible		Liu et al. 2009
Nd^{3+} , $\text{Nd}(\text{CH}_3\text{CO}_2)_3$	3.24	1 at.	14	visible		Liu et al. 2010(b)
Sb^{3+} , SbCl_3	-	0.03 mole	14			Omidi et al. 2013
V^{3+} , NH_4VO_3	3.17	10 at.	15-30	visible		El-Ghoul et al. 2012
Ti^{4+} ,	3.40	4 % wt.	25	-		Naeem et al. 2010

2.6 APPLICATION OF NANOPARTICLES SEMICONDUCTORS FOR PHOTOCATALYSIS

In the last two decades, the rapid growth in the population and industries has led to a greater demand for water for the continuation of life activities. Due to this growing request, some strategies have been suggested to make available more water resources. However, because of the decreasing amount of clean water, millions of people die annually from waterborne diseases (Malato et al. 2009). Such statistics are expected to rise in the future due to increasing water contamination. In order to avoid these problems, the water treatment process and development must be economically geared towards lowering the cost and raising the performance efficiency of water treatment.

Currently, the available processes of water treatment, such as adsorption and coagulation, can transfer the pollutant compounds onto another phase without any change to the structure of the compound (Padmanabhan et al. 2006). Moreover, other processes with higher costs such as sedimentation, membrane and filtration that are used for wastewater treatment also produce some toxic compounds as by-products (Gaya & Abdullah 2008). Various processes, such as electrochemical oxidation and photo-degradation by a suspension of metal oxide semiconductors (i.e. ZnO, TiO₂), have been suggested as efficient methods for solving this problem. However, this method is widely considered in this field because of the non-toxic nature of the final products and the higher efficiency and cheaper cost of the degradation process (Ohno & Tokeda 2003).

Photocatalysis is the acceleration of a chemical reaction by the absorption of light which activates a catalyst. Photocatalysis is comparable to natural photosynthesis, whereby both need energy by light radiation and a catalyst to accelerate the reaction. The adsorption of reactants to the photocatalytic surface is considered to be the main step for both photocatalysis and photosynthesis (Baruah et al. 2012). When the photocatalyst absorbs more energy than the band gap, the electrons are transferred from the valence band to the conduction band, where an electron-hole pair is formed in a very short time (few picoseconds). The reaction will occur within the formation of the electron-hole and there will be a loss of energy

within the recombination. Figure 2.13 gives a comparison of the mechanism between photocatalysis and photosynthesis. The photogeneration of electrons at the conduction band produces a superoxide, which then reacts with water to form hydrogen peroxide (H_2O_2). At same time, the photogenerated holes at the valence band will react with the organic molecules directly and convert them to CO_2 , H_2O and mineral salts.

Photocatalysis has many advantages, such as: (i) the reaction can take place at a low temperature (ambient temperature), (ii) several organic pollutants can be degraded in both aqueous and gaseous systems, and (iii) it is an inexpensive method for treating environmental contaminants (Demeestere et al. 2007). Photocatalysis is divided into two types, homogeneous and heterogeneous photocatalysis, according to the phase of the catalyst.

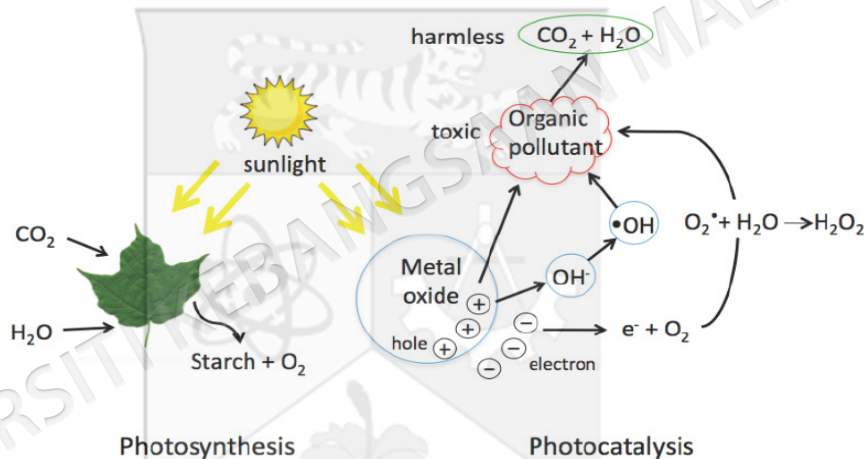


Figure 2.13 Comparison between the photosynthesis and photocatalysis under solar

Source: Baruah, et al. 2012

2.6.1 Homogenous Photocatalysis

This process favours a reaction when the reactants and catalyst are on one phase, where the photochemical reaction occurs in a homogenous solution. The ozone (O_3), transition metal oxide and photo-Fenton systems (Fe^+ and $\text{Fe}^+/\text{H}_2\text{O}_2$) are the most commonly used homogeneous chemicals (Aleboyeh et al., 2009). Additionally, the homogeneous process has some disadvantages such as the higher price of H_2O_2 and the increased operation cost involved in removing any material (organic and

inorganic) that may affect the performance (organic and inorganic). However, ozone is also limited in its mass transfer to water (low solubility) and would thus require some equipment that may increase the operation cost (Aleboyeh et al. 2009).

2.6.2 Heterogeneous Photocatalysis

In this process, the reactant and catalyst are on two or more phases from the start of the photochemical reaction. The first step in the reaction is the absorption of light by the catalyst and this usually takes place in a gas-solid interface for gas and a solid-liquid interface for aqueous systems. Semiconductors are the common materials that are applied for photocatalysis, where the band gap represents the difference in energy between the conduction band and the valence band (Herrmann 2005). When an electron leaves the valence band for a conduction band it creates a hole, $\cdot\text{OH}$, and other radicals will be produced by the oxidation of O_2 , H_2O and OH . Metal oxide particles, such as ZnO , TiO_2 , Fe_2O_3 and WO_3 are the photocatalysts that are used widely for the degradation of toxic environmental pollutants. These photocatalysts have different band gap energies which absorb light according to the wavelength as summarized in Table 2.5 (Stumm 1992). All semiconductors can be used as photocatalysts but only a few of them are shown good properties for the photocatalytic process. Generally, it has been reported that the best semiconductors are ZnO and TiO_2 , which have shown the highest efficiency for the degradation of large environmental pollutants (Han et al. 2012).

Table 2.5 Summary of band gap for most applied of semiconductors

Semiconductor	$E_g(\text{eV})$	$\lambda(\text{nm})$
CdS	2.4	517
Fe_2O_3	2.3	539
$\text{TiO}_2(\text{rutile})$	3.0	413
$\text{TiO}_2(\text{anatase})$	3.2	388
WO_3	2.8	443
ZnO	3.2	388
ZnS	3.6	344

2.6.3 Mechanism of Heterogeneous Photocatalysis

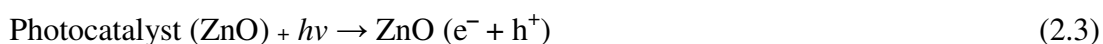
Heterogeneous photocatalysis is a photo-oxidation reaction in the presence of a photocatalyst. To improve the degradation efficiency, the three factors of light, photocatalyst and pollutants must be combined together. This process has been reported to change the reaction rate under ultraviolet, visible or infrared radiation in the presence of a photocatalyst and with light absorption (Braslavsky 2007). Generally, heterogeneous photocatalysis consists of five independent steps for the degradation process as follows (Herrmann 2005):

- (i) Diffusion of the pollutant molecules (reactants) from the bulk phase to the surface of the catalyst.
- (ii) Adsorption of pollutant molecules (reactants) onto the surface of the catalyst.
- (iii) A reaction that takes place in the adsorbed phase.
- (iv) Desorption of the products (intermediate compound) after the reaction.
- (v) Elimination of the final products from the interface region to the bulk fluid.

These steps have different effects depending on the experimental conditions such as initial concentration and amount of photocatalyst. Steps (i) and (v) are known as mass transfer, which depends on the concentration of the pollutant molecules (reactants) and the size of the photocatalyst. However, steps (ii), (iii) and (iv) are affected by the chemical properties of the pollutant molecules (reactants) and the final product molecules with active sites on the surface of the catalyst. Overall, one or more of these steps will control the chemical reaction rate, which requires finding the optimum condition for the process to achieve the maximum performance of the photocatalyst. Step (iii) is a very important step after the absorption of light by the photocatalyst, where the $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ reactive radicals are generated and act with the pollutant molecules to degrade them from the aqueous solution. Additionally, the photocatalytic oxidation has a sequence of steps which explains the mechanism of the oxidation reaction on the photocatalyst surface as given below (Hoffmann et al. 1995).

A. Charge-Carrier Generation

Upon photocatalyst, such as for ZnO lighting, where the energy is more than the band gap energy, the electrons are transferred from the valence to the conduction band with the creation of e^- and h^+ .



The electrons that are generated and held in the conduction band have a reduction power and oxidation takes place in the holes on the valence band which leads to a chemical reaction (redox). These electrons and holes are transferred to the photocatalyst surface and then react with the molecules that have been adsorbed on the surface.

(i) Charge-Carrier Trapping

Traps of the pair e^- and h^+ by the electron and the hole scavengers prevent them from recombining. There are two types of trapping as follows:

(ii) Hole trapping

The reactant adsorbed on the surface of the photocatalyst is gifted with a hole trapping, which can also be generated by a sacrificial chemical reagent. These trapped holes have been reported to directly oxidize the reactant molecules at the surface or generate higher oxidizing agents of $\cdot\text{OH}$ radicals (Hoffmann et al. 1995).



(iii) Electron trapping

Oxygen molecules are the best electron-trapping agents and during the reduction these combine with e^- and the reactive superoxide radical anions ($\text{O}_2^{\cdot-}$) are generated. Additionally, the process also produces other oxidizing species such as $\text{HO}_2^{\cdot}$ and H_2O_2 .

which increase the generation of $\cdot\text{OH}$ radicals (Carp et al. 2004). These reactions (charge-carrier trapping reactions) play a significant role in the photocatalytic degradation process.



(iv) Charge-carrier recombination

After the photocatalyst has absorbed the photon (light), the $\text{e}^- + \text{h}^+$ generation is very fast and then the trapping of the electrons and holes takes place. The $\text{e}^- + \text{h}^+$ recombination and carrier trapping are very important for the photocatalytic reaction, which can control the process efficiency (Hoffmann et al. 1995). However, the $\text{e}^- + \text{h}^+$ recombination has been reported as one of the main factors for controlling the rate of pollutant oxidation and follows the kinetics as a pseudo-first order under steady stated conditions (Carp et al. 2004). Generally, the recombination of $\text{e}^- + \text{h}^+$ on the surface of semiconductors is associated with the release of heat.



Generally, the best and strongest radical for the oxidation of organic compounds is the $\cdot\text{OH}$ radical, which has one of the highest oxidation potential exceeded only by fluorine as summarized in Table 2.6. These radicals react with pollutant molecules via two ways, i.e. by adding to their rings or by hydrogen abstraction from the alkyl or the substituted alkyl chain. The $\cdot\text{OH}$ radical is considered to be strongly electrophilic in nature, attacking the highest electron density of carbon atoms in aromatic compounds (Carp et al. 2004).

Table 2.6 Oxidation of oxidants

Species	Oxidation potential (V)	Relative oxidative power*
F ₂	3.03	2.23
•OH	2.80	2.06
O	2.42	1.78
O ₃	2.07	1.52
H ₂ O ₂	1.77	1.31
HO ₂ •	1.70	1.25
MnO ₄ ⁻	1.69	1.24
HBrO	1.59	1.17
ClO ₂	1.57	1.15
HClO	1.49	1.10
Cl ₂	1.36	1.00

2.6.4 Factors Affecting the Photocatalysis Process

Many operational conditions, such as photocatalyst loading, the initial concentration of pollutants, the pH solution and the intensity of light, affect the efficiency and reaction rate of the photocatalytic process. Additionally, the structure, morphology and characterization of the photocatalyst such as particle size, optical properties and surface area, also affect the efficiency of the process. To enhance the photocatalytic process, all the parameters should be optimized to make the process more economical by avoiding extra cost and operation time.

A. Photocatalyst Loading

The rate of the photocatalytic reaction (efficiency) is affected by the loading of the catalyst, where an increase in loading leads to an increased rate (Grzechulska & Morawski 2002). The efficiency is enhanced due to an increase in the total surface area as increased loading provides more active sites for the adsorption of molecules to increase the reaction rate. Loading above the optimal value will reduce the efficiency as the increased agglomeration of particles will cause a decrease in the available

surface area (active sites) for the molecules. Additionally, it has been reported that more particle suspension will lead to a reduction of light penetration with higher light scattering (Fujishima et al. 2007). The design of a slurry reactor is very important for optimal loading as it affects the penetration of light (Qamar & Muneer 2005). On the other hand, for an immobilized system, the optimal film thickness plays a main role in the photocatalytic efficiency and the thick films are good indeed for the degradation process.

B. Temperature

The temperature does not affect the photocatalytic degradation process because, unlike thermal reactions, the photodegradation reaction occurs at ambient temperatures (low activation energy, $5 - 20 \text{ kJ mol}^{-1}$) (Chen & Ray 1999). The temperature may possibly affect the adsorption and desorption of molecules, but it has no significant effect on the rate of the photocatalytic reaction within the range of $10-68^\circ\text{C}$ (Palmer et al. 2002). The photocatalytic reactions are slightly enhanced at higher temperatures as observed by Chen & Ray (1999). On the other hand, a higher temperature leads to a reduction in the dissolved oxygen concentration in water, and as such the photocatalytic removal of pollutants from water under almost ambient conditions has been recommended in the last decade (Tong et al. 2008).

C. pH of Solution

All the oxides of semiconductors have extensive effects on the rate of the photocatalytic reaction, which depends on the surface charge and the aggregation of the particles. Moreover, the photocatalytic reaction rate also depends on the properties or the behaviour of the pollutants (substrate) in various pH solutions. The zero point charge (pH_{zpc}) of ZnO is 9.0 and the surface of the catalyst is positive below pH 9 and negative if the pH is more than 9 (Sakthivel et al. 2003). Photocatalytic degradation increases with different charges on the catalyst surface and chlorophenols, for example (pH < pH_{zpc}), due to adsorption on the ZnO surface. However, when the pH > pH_{zpc}, the degradation rate becomes much slower because both the surfaces of ZnO and chlorophenols are negatively charged. Accordingly, the adsorption of

chlorophenols decreases because of the repulsive effect of the same charge between the surface of the ZnO and chlorophenol molecules. At a lower pH (pH 4), the ZnO is dissolved due to the amphoteric nature of the solution, while at a higher pH (pH 10) it forms zincates such as $\text{Zn}(\text{OH})_4^{2-}$ (Evgenidou et al. 2005). The overall efficiency of the photodegradation process can be determined under the optimum pH, which describes the behaviour of the process including the pollutants.

D. Initial Concentration of Pollutants

The initial concentration of pollutants is one of the main factors which control the reaction rate of photocatalysis. A higher adsorption of pollutant molecules on the surface of the catalyst is favoured to enhance the reaction by all the occupied active sites on the surface of the catalyst. An increase in the initial concentration of the pollutants can affect the adsorption up to a certain concentration, and these results may decrease the rate of the reaction. The optimum concentration is very important for the economical process to avoid a mass transfer limitation, which increases the rate of reaction with an increase in the mass transfer (Evgenidou et al. 2005). On the other hand, the intermediates that are produced after the reaction also affect the rate of reaction under a high concentration of pollutants. The initial concentration of pollutants is an important condition for the degradation process as reported earlier for different organic pollutants using ZnO powder (Lathasree et al. 2004; Pardeshi & Patil 2008).

E. Radiant Flux (solar intensity)

Solar technology has been widely used in heterogeneous photocatalysis (Malato et al., 2002). It has been shown in all types of photocatalysis that the reaction rate is proportional to the solar light intensity (radiant flux, Φ) and this is very important in choosing and designing a reactor. The highest activity in the photocatalytic process has been found to be typically that of a solar UV flux of 20 to 30Wm^{-2} ($0.2\text{-}0.3\text{ mol photons m}^{-2}\text{ h}^{-1}$ within a range of 300-400 nm) for sunny days and a concentration of sunlight is not suitable. Natural sunlight has been applied successfully for the degradation of many types of organic pollutants using ZnO particles, which were

developed by the heterogeneous photocatalytic process (Pardeshi & Patil 2009; Shinde et al. 2011). Figure 2.14 shows the solar spectrum with the visible region having the highest energy (43-46%) compared to other regions of UV (4-5%) and infrared light (Sakthivel et al. 2003).

The solar radiation that comes to the earth consists of two components, direct and diffused radiation. Direct radiation can be defined as the solar radiation that comes in a straight line from the source (sun) to the surface of the earth. On the other hand, diffused radiation can be defined as radiation that is scattered in the atmosphere by the presence of molecules or particles (such as some pollutants) before reaching the surface of the earth. When the sky is clear, about 85% of the direct radiation is in total isolation and about 15% is diffused (Masters 2004). The diffused radiation increases by up to 40% when the sun moves 10° above the horizon. The global UV radiation (direct + diffused) is higher than the direct radiation only and increases with atmospheric effects, such as prepared clouds or dust and humidity (Mehos & Turchi 1992).

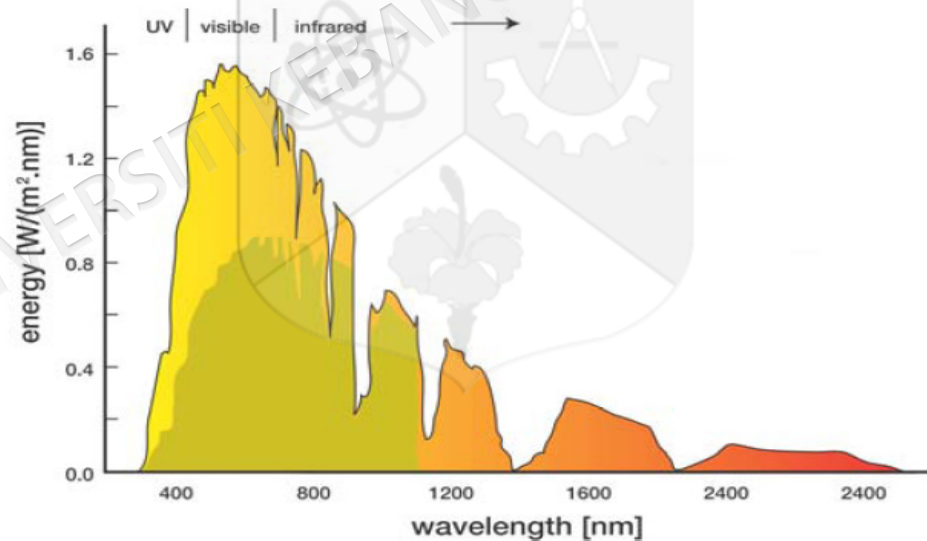


Figure 2.14 The solar spectrum and their comparison between UV and Visible

Source: Mehos & Turchi 1992

Diffused UV radiation reaches up to 50% of the total global radiation on a clear day and is reduced by scattering within the atmosphere because its UV

wavelength is shorter (Singh et al. 2011) as shown in Figure 2.15. The degradation of pollutants from water under solar irradiation on sunny days shows an enhancement in efficiency of up to 2–2.5 times higher compared to artificial irradiation (UV lamps) (Poulios et al. 1999). If the light source in industrial processes were to be replaced by sunny conditions, a degradation efficiency of more than 2.5 times would be obtained when compared to that of a cloudy day (Pardeshi & Patil 2008). Moreover, to enhance the recombination of the photo-generated electrons and holes in ZnO, the doping process has been devoted to shifting the absorbance from the UV to the visible region, where there is higher energy (Gaya & Abdullah 2008).

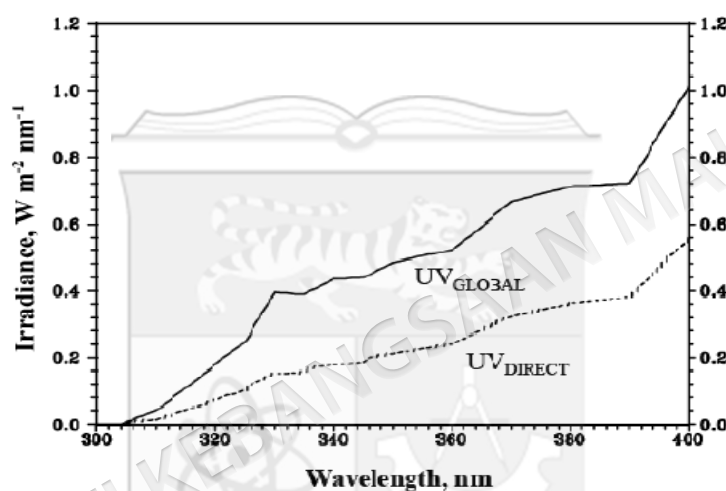


Figure 2.15 Comparison of global and direct UV of solar on earth surface

Source: Priya, et al. 2008

2.6.5 Surface Morphology and Structural Properties of ZnO

The activity of ZnO for the photocatalytic process is more significant in terms of the surface and structural properties such as the crystal structure, surface area, and particle size.

A. Crystal structure and surface area of ZnO

The wide ZnO band gap makes it capable of absorbing a larger fraction of the solar spectrum than TiO₂, and therefore it has been suggested that the ZnO photocatalyst is the preferred choice for the photocatalytic degradation under direct sunlight

(Karunakaran & Dhanalakshmi 2008). ZnO is commonly used as a semiconductor for photocatalysis because of its hexagonal wurtzite crystalline structure. The hexagonal wurtzite structure of ZnO is more stable than other structures (cubic zinc blende, cubic rock salt) under ambient conditions (Wang 2004). However, the surface area is the most important factor for improving the photocatalytic process by increasing the adsorption of molecules and the rate of reaction. The photocatalyst has a higher surface area which leads to an increase in active sites for adsorbing pollutant molecules and oxygen, which then enhance the rate of reaction. The maximum photocatalytic activity can be obtained by maintaining a balance between the surface area and the crystallinity of the catalyst.

B. Particle sizes of ZnO

Particle size plays a main role in the heterogeneous photocatalytic process using semiconductors, which are related directly to a specific surface area of the photocatalyst. Moreover, the particle size also controls the electron/hole recombination process, which affects the activity of the photocatalyst (Baruah et al. 2010). Generally, the properties (physical and chemical) of nano-sized ZnO are modified for applications compared to the bulk (Nair et al. 2011). Small changes to the size of particles can result in higher modifications on the surface electron/hole recombination that can improve the photoactivity process. The number of active sites increases with a decrease in the particle size, with the rate of mass transfer enhancing the photocatalytic process (Baruah et al. 2010).

2.6.6 Photocatalytic Degradation of Organic Pollutants Using ZnO

Wastewater contains phenolic compounds such as chlorophenols (CPs), which have been reported to be priority toxic pollutants in industries (Keith & Telliard 1979). Chlorophenols (CPs) are listed as toxic by the US EPA in The Clean Water Act and by the European Decision 2455/2001/EC (EC Decision 2455/2001/EC). These compounds can be found in groundwater, soils and wastewater and they have negative effects on the environment even when present in very low concentrations (0.1 µg/L) (Veschueren 1983). Various human activities produce several types of CPs such as

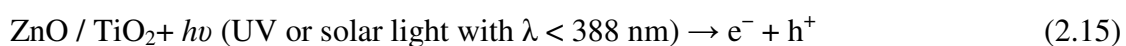
vegetable fibres, paints, leather and disinfectants. However, CPs are used in some industrial processes such as in the manufacture of pharmaceuticals, herbicides, pesticides, insecticides and fungicides, and can be found as a by-product of certain processes such as the dechlorination of drinking water and the bleaching of pulp (Pandiyan et al, 2002; Lathasree et al., 2004). Generally, monochlorophenol compounds are used to produce chlorinated phenols and dyestuff, and 2,4-dichlorophenol (DCP) is also used as a main compound to produce 2,4-dichlorophenoxyacetic acid. However, 2,4,6-trichlorophenol is an important compound for the production of 2,4,6-trichlorophenoxyacetic acid (Pandiyan et al. 2002).

Table 2.7 Types of CPs in drinking water

CPs	($\mu\text{g/L}$)	<i>Daphnia magna</i> 24 hr, (mg/L)
2-MCP	0.1	16.60–19.30
3-MCP	0.1	13.80–17.79
4-MCP	0.04	5.79–10.34
2,3-DCP	0.1–1.00	4.09–6.30
2,4-DCP	0.5	2.48–2.89
2,5-DCP	0.2	-
2,6-DCP	0.3	8.69–10.08
3,4-DCP	1.0	2.55–2.98
3,5-DCP	-	1.85–2.33
2,3,4-TCP	-	2.00–2.48
2,3,5-TCP	-	2.06–2.50
2,3,6-TCP	-	6.25–8.52
2,4,5-TCP	0.1–2.00	1.88–2.29
2,4,6-TCP	-	4.93–6.01
3,4,5-TCP	-	0.82–0.93
2,3,4,5-TTCP	-	1.52–1.98
2,3,4,6-TTCP	1.00	-
2,3,5,6-TTCP	-	1.87–2.66
PCP	3.0	0.62–0.89

All CPs have a higher toxicity in organisms which increases with an increase of chlorine in the phenol ring or a substitution starting in the ortho-(2-) position (Marc et al. 2004). The toxicity of CPs has been attributed to an increase in lipophilicity, which has a higher potential of uptake into the organism. For example, the ortho-(2-) position has a lower toxicity than others (meta-and para) because the ortho-substituted chlorine works to shield the OH group. Table 2.7 summarizes all the types of CPs with the permissible amounts in drinking water with the range of toxicity on *Daphnia magna*.(Devillers, & Chambon 1986) On the other hand, CPs such as 2-chlorophenol (2-MCP), 2,4-dichlorophenol (2,4-DCP) and pentachlorophenol (PCP) in surface or groundwater should not be more than 2.020, 4.380 and 0.055 mg/L (Jones & Watts 1997).

In the last two decades, a new way has been reported to completely remove CPs from aqueous solutions by Advanced Oxidation Processes (AOPs) using heterogeneous photocatalysis. Recently, the focus has been on the generation of highly reactive hydroxyl radicals ($\cdot\text{OH}$) on the surface of a photocatalyst due to their ability to destroy CPs in water to produce a nontoxic product under ambient processing conditions (temperature and pressure) (Ahmed et al. 2011). The two semiconductors that are commonly used as photocatalysts and which are suitable for the degradation of many organic pollutants are ZnO and TiO_2 . These photocatalysts have a higher activity and stability under operating conditions of the process and a low cost of production (Rao et al. 2009). As ZnO and TiO_2 are absorbed, the energy increases to more than the band gap (3.2 eV) by using a UV lamp or solar light, and a strongly reactive species is generated. The excitation of the electron (e^-) from the valence band to the conduction band will generate holes on the valence band (h^+). Sequentially, the anion radicals ($\text{O}_2^{\cdot-}$) produced from the electron will react with the oxygen adsorbed on the catalyst surface and the hydroxyl radicals ($\text{OH}^\bullet$) from the hydroxide anions (OH^-) with holes (Ahmed et al. 2011). The oxidation pathway mechanisms of ZnO and TiO_2 are similar for the generation of the strong reactive radicals as below:





In countries that have sufficient quantities of sunlight, the use of sunlight for the photocatalytic process has become easy and economically acceptable. Hence, the degradation of the pollutants from water under solar irradiation on sunny day enhances the efficiency by up to 2–2.5 times compared to artificial irradiation (UV lamps) (Poulios et al. 1999). If sunny conditions were to replace the light source in industrial processes, a degradation efficiency of more than 2.5 times would be obtained when compared to during cloudy days (Pardeshi & Patil 2008). Hence, solar light on sunny days was used to conduct the experiments in this study as the cost is lower and it is an environmentally-friendly source of energy. The photodegradation process under solar radiation has been used for two types of photoreactors, the concentrating and non-concentrating photoreactor. The concentrating reactor has a disadvantage in that it cannot concentrate diffused radiation and can only use the total solar radiation directly (Toor et al. 2005). At same time, the non-concentrating photoreactors, such as shallow solar ponds and slurry, use total solar radiation including direct and diffused radiation, and they have a simple design for the scale up, low construction cost and are easy to maintain (Pozzo et al. 1997).

Recently, a comparison between artificial UV and solar light for the degradation of organic pollutants using ZnO and TiO₂ reported that ZnO is more efficient than TiO₂ under solar radiation (Han et al., 2012; Fenoll, et al. 2011). The applications of ZnO nanoparticles for the degradation of organic pollutants such as phenol, polychlorophenol and others with the important conditions for the process are summarized in Table 2.8.

Table 2.8 Photocatalytic degradation of various organic pollutants using ZnO with different conditions

Pollutant name	Light source	Best loading g/L	pH	Reference
Phenol	Solar	2.5	5.0-6.0	Pardeshi & Patil 2008
Phenol	Solar	2.0	5.0	Parida & Parija 2006
Phenol	UV	2	6.0	Sun et al. 2011
Phenol	UV	2	6.0-7.0	Anju et al. 2012
Phenol	UV	2.5	5-6	Hayat et al. 2011
phenol	UV	2	7.0	Lathasree et al. 2004
phenol	UV	2.0	5.0	Shukla et al. 2010
Phenol	UV	1	6	Devipriya & Yesodharan 2010
Phenol	UV	1	6	Liqiang et al. 2006
4-Nitrophenol	Solar	1.5	6.0	Parida & Parija 2006
4-Nitrophenol	UV	0.3	7	Tabatabaei, et al. 2011
2,4-dinitrophenol	UV	2	6	Vora et al. 2009
4-chlorophenol	UV	1.2	7	Ou et al. 2006
4- chlorophenols	UV	1.5	6	Hariharan 2006
4-chlorophenol	UV	1.5	7	Gaya et al. 2009
2-chlorophenol	UV	2	7.0	Lathasree et al. 2004

Continue...

...Continued

2,4-dichlorophenol	artificial solar light	2	5.0	Shukla et al. 2010
2,4-dichlorophenol	UV	1.5	6-7	Gaya et al. 2010a
2,4,6-trichlorophenol	artificial solar	0.4-2.0	5.0	Shukla et al. 2010
2,4,6-trichlorophenol	UV		7	Huang et al. 2005
2,4,6-trichlorophenol	UV	1	5.5	Anandan et al. 2007(a)
2,4,6-trichlorophenol	UV	-	6	Abdel Aal et al. 2009
2,4,6-trichlorophenol	UV	1	6.5	Gaya et al. 2010b
Amoxicillin,	UV	1.5	11	Elmolla & Chaudhuri 2010
Ampicillin Cloxacillin				
Salicylic acid	UV	2	7.0	Rao et al. 2009
metamitron	UV	2	6.2	Mijin et al. 2009
ciprofloxacin drug	UV	-	7	El-Kemary & El-Mehasseb 2010
Estrone	Solar	1	10	Han et al. 2012
Pesticides,	Solar	1.5	6-8	Navarro et al. 2009
Azoxystrobin				
Cyprodinil Fludioxonil	Solar	1	6-8	Fenoll et al. 2011
Phosphamidon	UV	1.25	6-6.5	Rabindranathan et al. 2003

Continue...

...Continued

S-triazine	Solar	1	6	Fenoll et al. 2012(a)
Chloroacetanilide				
herbicides				
Monocrotophos	UV	1	5.5	Anandan et al. 2007(b)
Carbofuran	Solar	1.5	6-8	Fenoll et al. 2013
Dichlorvos	UV	1.5	7	Evgenidou et al. 2005
Diazinon	UV	3	5.2	Daneshvar et al. 2007
Terephthalic acid	UV	2.5	9	Shafaei et al. 2010
Resorcinol	Solar	2.5	9	Pardeshi et al. 2009
Fenamiphos	Solar	1.5	6-7	Fenoll et al. 2012(b)
Pentafluorobenzoic acid	UV	1.5	5	Ravichandran et al. 2007
Remazol Red	UV	3.5	10	Akyol et al. 2004
Acid black 1	Solar	6	9	Krishnakumar & Swaminathan 2010
Acid brown 14	Solar	2.5	9	Sakthivel et al. 2003
Methylene blue	UV	5	9	Venkatesham et al. 2012
Thionine	UV	2	-	Khayyat et al. 2012
acid red 18	UV	4	11	Sobana & Swaminathan 2007

2.7 DESIGN OF EXPERIMENTS (DOE) FOR ZnO SYNTHESIS AND PHOTOCATALYSIS APPLICATIONS

ZnO is known to have a large direct band gap of 3.37 eV and a large excitation binding energy of 60 meV (Hong et al. 2009). ZnO is commonly used as a semiconductor and may be obtained in the form of a hexagonal wurtzite crystalline structure. ZnO nanoparticles have been applied in photocatalysis, sensors and desensitized solar cells because of their good optical, electrical and chemical properties (Sheng et al. 2007). The principal methods commonly used to synthesize ZnO nanoparticles are precipitation, spray pyrolysis, hydrothermal synthesis, electrochemical and sol-gel methods (Hou et al. 2008). ZnO nanoparticles, which have an excellent crystalline structure and a narrow size distribution, have been synthesized using the sol-gel process with zinc acetate as a starting material (Kim et al. 2002). Compared to all these methods, the sol-gel process is the most attractive method as it can be performed in a relatively straight forward way and it allows improved control of the particle morphology via the rate of hydrolysis and the condensation reactions.

A capping agent or a surfactant was used in an earlier study in order to control the size of the semiconductor nanoparticles (Kim et al. 2006). Capping agents such as thiophenol and mercaptoacetate (Wageh et al. 2003; Amma 2006) are toxic chemicals and are difficult to completely remove from the surface within the synthesized process, thus making it difficult for the large-scale production of nanoparticles that could contaminate the environment. The molar ratio of the starting material had earlier been adjusted to investigate its effect on controlling the size and shape of the produced nanoparticles (Dios et al. 2005), while other studies (Alias et al. 2010) developed nanoparticles of different sizes by adjusting the pH of the solution. In addition, it has been reported that the type of solvent used has an effect on the surface morphology and properties of the ZnO nanoparticles (Uthirakumar & Hong 2009). Organic solvents, such as methanol and ethanol, have been reported (Zhang et al. 2002) to be the best solvents for reducing the size of ZnO nanoparticles due to their ability to control the nucleation process and its crystal orientation.

2.7.1 Design of Experiments (DOE)

Design of experiment (DOE) is an interesting way to evaluate and solve problems in scientific studies. The aim of a DOE is to produce a model with a good explanation of all the conditions of the case study. In order to develop a final model of any process, it is necessary to have significant information about a case study, such as the interaction between the parameters (independents factors). Different experiments are conducted according to the DOE to find a process model that gives the best performance in order to develop an overall process for the future. The information from the target study can be observed by experiment, and the hypothesis can be verified or falsified by the investigation of experimental tests. The DOE is used to optimize the process parameters by performing the experiments and explaining the significant behaviour of the process according to the results. The DOE is an economical and effective way to solve the problem statement of a study by minimizing experiments for combination factors to as low as possible due to cost considerations (Wu & Hamada 2000).

In order to evaluate the experiments using the DOE, there must always be two variables called the factor and the response. The factor manipulates the response which also gives the information for the performance of the process or the system. Factors can be set on a range of values (more than two) and can also be divided into groups. A response results from changing the factors of a process, where it is possible to measure multiple responses at the same time. The relationship between the factor and the response of a process is shown in Figure 2.16.



Figure 2.16 Relationship between the factors and responses within the process

Source: Eriksson et al. 2000

A. Model concept

The DOE helps to create a mathematical model which is important for investigating the system or the process using the selected factors and responses. The final model is not 100% correct, but at same time it is simply meant to transfer the complexity of the real conditions into equations which are easy to use (Eriksson et al. 2000). A linear model is the simplest model in which the factors $\chi_1, \dots, \chi_i$ influence the response, y , in the following equations given below:

$$y = \beta_0 + \beta_1 \chi_1 + \dots + \beta_i \chi_i + \varepsilon \quad (2.22)$$

where $\beta_0, \beta_1, \dots, \beta_i$ are the regression coefficients, and ε is a random part of the model and is assumed to be 0. When multiple responses are used, the equation becomes:

$$y_i = \beta_0 + \beta_1 \chi_{i1} + \dots + \beta_i \chi_{ij} + \varepsilon, \quad i = 1, \dots, N \quad (2.23)$$

where y_i is the response for $\chi_{i1}, \dots, \chi_{ij}$. The matrix of all the equations can be represented as:

$$Y = X \beta + \varepsilon \quad (2.24)$$

where the X model of the matrix contains all the factors affecting the response, and β is the regression coefficient for unknown parameters in the model. The experiments should help in the selection of a model, which could be a linear model, or other mathematical models such as interaction or quadratic models.

$$Y = \begin{bmatrix} y1 \\ . \\ yN \end{bmatrix}, \quad X = \begin{bmatrix} x11 & \cdots & x1j \\ \vdots & \ddots & \vdots \\ xN1 & \cdots & xNj \end{bmatrix}, \quad \varepsilon = \begin{bmatrix} \beta1 \\ \vdots \\ \beta N \end{bmatrix} \quad (2.25)$$

B. Experimental Objectives

The main part of the DOE is the objective (purpose) of the experiment, which is to create the design, and there are two important types of designs in this aspect:

(i) Screening

The performance of a process is investigated by experiments using the screening design first to determine the main factors and their varying effects on the response of the process (Montgomery 1991). The main objective of the screening design is to identify the significant factors rather than their interaction, and usually the screening design uses a large number of input factors to enhance the analysis of the design. The determination of the significant factors can help in the next step, which is the optimization of the process, by considering only those factors that greatly affect the process.

(ii) Optimization

Optimization is required after the significant factors of the process have been identified by the screening design. In the optimization design, the effects of factors and their interaction lead to the production of the best response with detailed information from the experiments. This simply means that the design helps to create a model to optimize the process by finding an optimal experimental target point from predicting the values of responses within possible interactions between all factors (Montgomery 1991). An estimation of the interactions between the factors by response surface modelling (RSM) has been reported with investigations into the shape of the response surface of the final results (Wu & Hamada 2000). Therefore, RSM improves the optimization process and enables one to find a good interaction of input factors which then leads to the best response (output).

2.7.2 Response Surface Methodology (RSM)

Response Surface Methodology (RSM) is a statistical technique used for the designing of experiments and the building of experimental models involving many interactive parameters. In addition, RSM has been utilized to evaluate the relationship between multiple independent variables (factors) and to determine the optimum conditions required to produce a specific desired response (Box & Draper 1987). Classically, RSM approaches not only evaluate interaction effects between selected variables but

also reduce the number of experimental runs that need to be performed (Karacan et al. 2007). The optimization of any process parameter is performed on the final product, which increases its importance in applications. The experimental design and optimization of ZnO nanoparticles have earlier been evaluated using RSM (Uthirakumar & Hong 2009).

To apply the RSM for the optimization of the process, firstly, the design of the experiments must be selected so as to identify which experiments should be studied in the region. For example, the first order model, such as a factorial design, must be used according to the data set as a linear function and not as a curve. At same time, the data of the response cannot be examined by a linear function. Quadratic response surfaces are used for descriptions such as central composites, Box–Behnken, three-level factorial, and D-optimal designs (Gilmour 2006). The general steps that are followed for the optimization technique using RSM are summarized below as: (1) Selection of major significant factors affecting the process or system within the screening study and determining the region of the experiments according to the objectives of the study or of previous studies; (2) Selection of an experimental design that is suitable for a case study and that is carried out according to the selected design matrix; (3) Treatment of the experimental data by mathematics and statistics during the fitting of polynomial functions; (4) Evaluation of model fitness and verification for optimal conditions; and (5) Determination of optimal conditions for the study

A. Screening of variables

The first step in building the model of the process is to screen the independent variables (factors) that have a more significant effect on the selected response of the process. The screening identifies the significant experimental variables and their interactions which lead to the development of the application process. Usually the two-level factorial, full factorial and Plackett Burman designs are applied for the screening of the effective variables because these are efficient and economical designs (Teofilo & Ferreira 2006).

B. Select of the design

The linear model is the simplest model used in the RSM, which is important for finding a well-fitted response according to the equation:

$$y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \varepsilon \quad (2.26)$$

where k is the factor number, β_i is the coefficient, x_i is the factor and ε is the residual. However, the second order model is used to investigate the curvature of the two-level factorial designs (polynomial) with central points. In this model, the interactions between the factors of the experiment are explained as:

$$y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{1 \leq i \leq j}^k \beta_{ij} x_i x_{ij} + \varepsilon \quad (2.27)$$

where, β_{ij} is the coefficient of the interactions of factors. To evaluate the maximum and minimum points of the model, it is very important to add the quadratic terms to the polynomial functions according to the equation below:

$$y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum_{1 \leq i \leq j}^k \beta_{ij} x_i x_{ij} + \varepsilon \quad (2.28)$$

where, β_{ii} is the coefficient of the quadratic terms. To evaluate all the parameters of Eq. (2.7), the design of the experiment should be run in at least three factor levels (Gilmour 2006). The second order designs that are commonly used are the central composite design (CCD), the Box–Behnken design, the three-level factorial design and the D-optimal design. All these designs are different in respect to the selection of the number of levels of the factors, experimental points, number of experimental runs and number of blocks.

C. Evaluation of the fitted model

After a model is found that fits the function, the application of an analysis of variance (ANOVA) is used to evaluate the final fit of the model. The purpose of the ANOVA is

to compare the variation within the treatment with the variation within the random errors associated with the measurement of the responses (Gilmour 2006). This step creates the significance of the model regression to evaluate the response from the sources of the experimental variance. The ANOVA includes some terms such as the total sum of the square (SS_{tot}) which is the sum of the square of the deviations (di) of observation (y_i) or its replicates (y_{ij}) that relate to the study (y^-) as in the equation below:

$$d_i^2 = (y_{ij} - y^-)^2 \quad (2.29)$$

Moreover, the total sum of the square (SS_{tot}) is divided into the sum square results from the fitted model mathematically due to the regression (SS_{reg}) and the sum square as the residual results from the model (SS_{res}) as given below:

$$SS_{tot} = SS_{reg} + SS_{res} \quad (2.30)$$

The sum square of the residuals is calculated from two different sum squares, i.e. the sum square of pure errors (SS_{pe}) (due to replicates of the experiments) and the sum square due to lack of fit (SS_{lof}) as given below:

$$SS_{res} = SS_{pe} + SS_{lof} \quad (2.31)$$

D. Evaluation of the optimization conditions

The optimization condition of any process is very important as it controls the levels of the factors that can produce the best value of the response. The “trial-and-error” method, which is used as a traditional method, has a lot of disadvantages such as lower interaction effects between the factors and lower efficiency to produce the true optimum value of the response. The RSM is a simple and efficient method to obtain the exact optimum value. According to the RSM, second-order models have quadratic surfaces which are different such as minimum, maximum, ridge and saddle (Gilmour 2006). The conical surface analysis of the second-order model when it is according to

Equation (2.7) can help to determine the optimal points. The optimal points are the combination of design factors, where the surface in all directions is either maximum or minimum. The saddle point can be found when the optimal points are not at the same level as the maximum in some direction and the minimum in another direction.

Another type of surface, which is known as the ridge system, occurs when it is curved in one direction and fairly constant in the other (Oehlert 2000). These surfaces describe the optimization of the predicted model using the 3-dimensional surface of the response and also the contour plots. For the optimization of the process responses, the desirability function (D) has been applied as a well-known technique to optimize the performance of the factor levels. This technique has been developed and modified for describing the relationship between the factors that predict the response and the response desirability. The range of the desirability is from zero (minimum value) to one (maximum value) with the value that is close to one as the target goal. The maximum value reflects the importance of the factors for the required results of the experiments.

2.7.3 Second-order Experimental Designs

To estimate the process model, the suitable DOE using the RSM greatly affects the building of a highly accurate process response. The most famous RSM designs that are used for process optimization are described individually below.

A. Full Three-level Factorial Design

In general, the full three-level factorial design has three levels, low, centre and high, which can be applied for the process factor. The number of experimental runs (calculated by $N=3^k$, where N is the experimental runs and k is the number of factors) by applying this design is very large and influences the efficiency of the model. If a process has more than two factors that need to be investigated, then more experimental runs are required and these can be reduced by using the suggested designs such as the Box–Behnken, central composite and D-optimal designs (Morris 2000).

B. Box–Behnken Designs

The Box–Behnken design is a three-level factorial design for three factors with selected points from a system arrangement (Box & Behnken 1960). The number of experimental runs required (N) is calculated by $N=2k(k-1) + C$, where the number of factors is k and the centre point is C . The advantage of this design is that it can reduce the runs and can be used for a large number of factors according to the $3k$ design. To improve the performance of the Box–Behnken design, the three levels ($-1, 0, +1$) of the factors should be adjusted with $N=2k(k-1) + C$ number of experimental runs.

C. Central Composite Design

A central composite design is applied for second-order response surfaces and was first presented by Box and Wilson (Box & Wilson 1951). This design consists of a fractional factorial design and additional experimental points from the centre as well as the centre points. However, the number of experimental runs can be calculated by $N=2^k + 2k + C$. The central composite design has a distance from the centre point called α , which depends on the selected factor number of the experiments. However, the different values of α are according to the factor numbers. For example, 1.41, 1.68 and 2.00 are for the two, three and four factors, respectively. The five factor levels ($-\alpha, -1, 0, +1, +\alpha$) produce larger experimental runs and this is considered to be a drawback of the central composite design.

D. D-optimal designs

The DOE has been used for three regular designs, the central composite design (CCD), the Box–Behnken design and the full three-level factorial design, as standard designs. However, another design, known as the D-optimal design, has been applied for certain cases and situations (Myers & Montgomery 2002). This design is generated for the following situations:

(i) The region of the experiment is irregular

The region of an experiment is determined by the choice of factors which can influence the shape of the final area of the design (Eriksson et al. 2000). All of these areas (such as the quadratic and cubic areas) do not constrain the formulation of the final problem of the designs. The example in Figure 2.17(a) shows a quadratic design in which one of the corners is not included. Therefore, this design cannot be applied because this corner is out of the range of influence. The D-optimal design appears to be the best method to solve this problem, where the algorithm selects two points on a constrained border without the corner. Accordingly, the centre point is manipulated (Eriksson et al. 2000).

(ii) Experiments that have already been performed have to be included.

In many cases, the researcher has done a number of experiments and would like to add all the findings into his investigation design. In this case, it is not possible to use a conventional design (central composite design, Box–Behnken design or full three-level factorial design) to add the findings of the experiments to the design. At the same time, the addition of runs as part of the design is possible with the D-optimal design and the findings of experiments can be considered throughout the creation of the design (Eriksson et al. 2000).

(iii) Number of factors and reducing the design runs.

The number of process factors is important in determining the runs of experiments at discrete levels. Usually, when the level of factors becomes more than two, the runs of experiments increase drastically according to the levels of each factor. Figure 2.17 (b) shows the four and three levels of process factors and the design of the process experiment using the full factorial design. Accordingly, the D-optimal design reduces the runs of these process experiments to half as shown by the black-filled circles in Figure 2.17 (b).

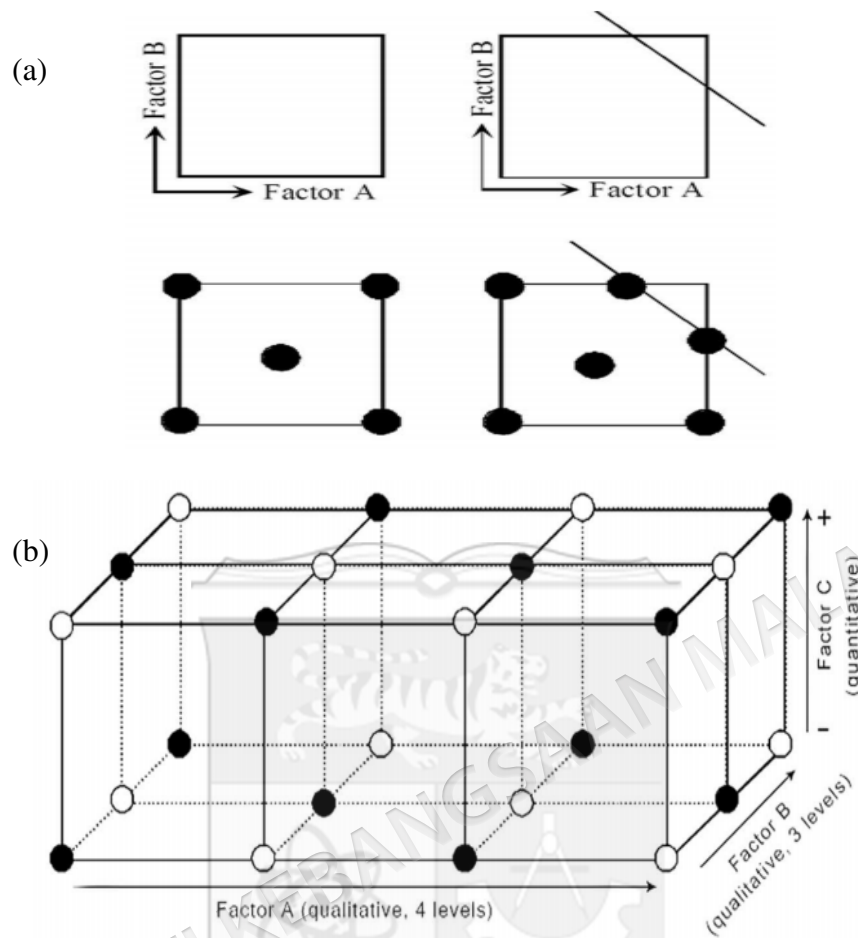


Figure 2.17 (a) D-optimal algorithm selection (b) D-optimal reduces runs

Source: Eriksson et al. 2000

These experimental runs are selected to guarantee that the design covers all regions of the experiment (Eriksson et al. 2000). On the other hand, the traditional designs are more affected by the number of factors, where increasing the number of factors increases the experimental runs. In c, a lower run of experiments is always achieved by the D-optimal design compared to a full factorial design, where there is no fast increase with a rise in the number of factors, as with traditional designs. A comparison of the factor number with experimental runs with D-optimal and traditional designs are summarized in Table 2.9.

Table 2.9 Comparison of experiment runs according of number of factors

Factor number	Full Factorial	CCD	Box–Behnken	D-optimal
3	8	20	17	18
4	16	30	29	25
5	32	50	46	31
6	64	86	54	38

Recently, an empirical equation was applied and developed for many applications in the industrial field. The response surface methodology (RSM) is used to determine the effectiveness and robustness of a design according to the selection of more significant points from the general points for an adequate and satisfactory region of the design. The D-optimal design (D = dispersion matrix) fits these criteria sufficiently when compared to other designs such as the Box-Behnken design and the central composite design (CCD) (Hasan et al. 2012). The building of an algorithm in the D-optimal design provides a highly accurate estimation for the coefficients of the model (Korbahti & Rauf 2009).

The selection of the D-optimal design according to the minimization technique involves three main steps: (i) level definition, (ii) suitable model selection, and (c) choice of design points from a set of candidate points that have been considered for use by experiments depending on the model (Grcic et al. 2010). In general, the candidate points are a grid of points spaced over a feasible design. The D-optimal design is one of the more popular and efficient constructions for a quadratic model (Myers & Montgomery 2002). One of the advantages of this design is that the number of experiments is specified by the selection of certain points from a large set of candidate points. The matrix of the D-optimal design is expressed below:

$$Y = X * B + \varepsilon \quad (2.32)$$

where Y is vector of observations (response), X is the matrix value of D-optimal design factors and B is vector of regulation of factors and ε is errors. The B is evaluated using the least - squares method as shown below:

$$B = (X^T * X)^{-1} X^T Y \quad (2.33)$$

The best set of experimental points is maximized by the determinant $|X^T X|$, in which the “D” stands for the matrix determinant $|X^T X|$ related to the model. The maximum variance of the predicted responses of the process is minimized using the D-optimal design, in which the experimental points can minimize the error of the coefficients of the response model. To use this design, the optimal distribution of the experimental points selected from the total, which can be given with the determinant $X^T X$, is maximized. Over the last five years, the D-optimal design has been commonly applied to select an optimal set of experiments by analysing the data variance for different applications, such as for the photocatalytic degradation of phenol and dyes, and for chromatographic and fluorescence techniques as given in Table 2.10 and 2.11.

2.7.4 RSM Design for Optimization of Photocatalytic Process

In the last two decades, the promising technology of photocatalysis has been applied for the degradation of many organic pollutants from industrial wastewater. However, a few studies have focused on the use of statistical designs to optimize experiments on the photocatalytic degradation process. To find a final target response as an appropriate way to optimize the experimental conditions, the RSM has been used to determine which specific factors and conditions are more significant (Korbahti & Rauf 2009). In addition, the RSM has been utilized to evaluate the relationship between multiple independent variables (factors) and to determine the optimum conditions required to produce a specific desired response (Korbahti & Rauf 2009).

Classically, RSM approaches not only evaluate the effects of interaction between selected variables but also reduce the number of experimental runs that need to be performed (Karacan et al. 2007). RSM is the best application for the development of industrial processes which optimize and control the final product according to the targeted properties which are very important for the overall process (Box et al. 2005). Several studies have applied experimental statistical designs to

optimize the photocatalytic process. A statistical design is an important way to develop a process in industrial research.

Generally, for the screening of the most significant process factors, the two-level full factorial, the Plackett Burman, and fractional factorial (Teofilo & Ferreira 2006) designs have been used. For the optimization of significant factors of the process, the main RSM designs have been used such as the central composite, Box-Behnken, three-level full factorial and D-optimal designs (Gilmour 2006). Table 2.10 summarizes the many studies that have used the RSM based on the D-optimal design and others for the optimization of the photocatalytic degradation of chlorophenols and colour pollutants including the ZnO and TiO₂. The application of this process is affected by factors such as the amount of catalyst, the pH of the solution, the concentration of pollutants, UV and solar light.

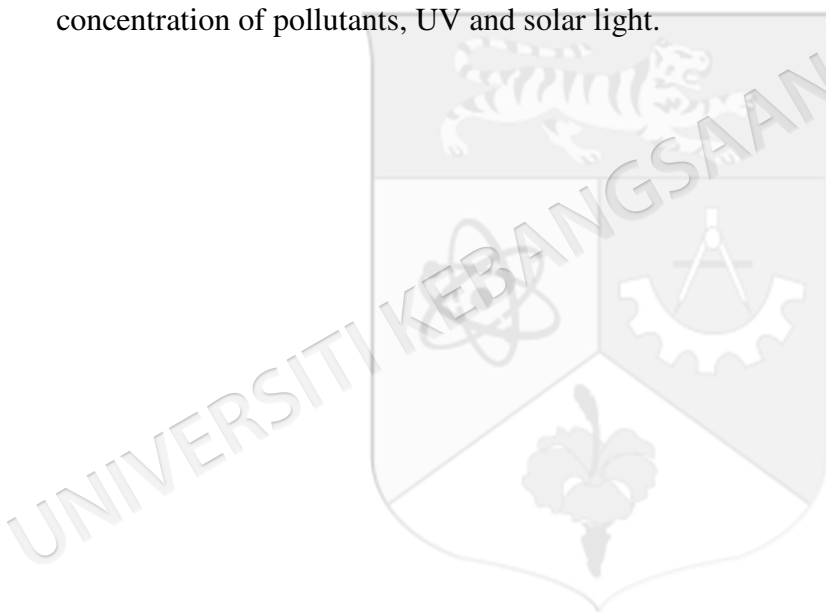


Table 2.10 Optimization of photocatalytic degradation for different pollutants using RSM

Pollutant name	Variables of Photocatalytic process	RSM for optimization process	Instrument for analysis	Reference
Phenol	TiO ₂ , ZnO, pH, phenol concentration, catalyst dose	2 ³ factorial	Luminescence spectrometer	Bosco & Larrechi 2008
Phenol	Phenol concentration, catalyst dose, hydrogen peroxide, Time	D-optimal	Spectrophotometer	Ayodele et al. 2012
Phenol	pH, phenol concentration, reaction temperature, UV irradiation time, UV light intensity, catalyst calcination temperature, dosage of TiO ₂ /perlite	D-optimal	Spectrophotometer	Jafarzadeh et al. 2011
p-chlorophenol	pH, Fe ³⁺ , C ₂ O ₄ ²⁻ , UV	Box-Behnken	HPLC	Kusic et al. 2011
4-chlorophenol	ZnO doses, 4CP concentration	Central Composite	Spectrophotometer	Gaya et al. 2009
2,4-Dichlorophenol	Catalyst dose, pH, oxidant concentration.	Central Composite	HPLC	Kansal et al. 2009
2,4-Dichlorophenol	Agitation speed, pH Contact time, concentration	Central Composite	Spectrophotometer	Alam et al. 2007

Continue...

...Continued

2,4,6-trichlorophenol	TiO ₂ dose, pH, oxidant concentration	Central Composite	HPLC	Kansal et al. 2007(a)
Catechol	TiO ₂ dose, pH, oxidant concentration under UV and sun light	Central Composite	Spectrophotometer	Kansal et al. 2007(b)
Azo dye acid green 20	power density, pH dye and H ₂ O ₂ concentration	Box-Behnken	Spectrophotometer	Zhang & Zheng 2009
Flumequine	TiO ₂ , urea, thiourea, pH ,catalysts dose under solar	Central Composite	Spectrophotometer and HPLC	Nieto et al. 2008
Tetracycline	TiO ₂ , ZnO, Catalyst dose, pH	Central Composite	Spectrophotometer	Palominos et al. 2009
Reactive Blue 19	TiO ₂ , ZnO,dose, pH, dye concentration	Factorial design	Spectrophotometer	Lizama et al. 2002
Azo Dye	TiO ₂ t dose, pH , reaction time. under sun light	Central Composite	Chemical Oxygen Demand,Total Organic Carbon	Kuo & Chen 2012
Basic Red 2(BR2)	H ₂ O ₂ ,BR2 concentration, pH	D-optimal	Spectrophotometer	Bahadir & Rauf 2008

Continue...

...Continued

Carmines (C.I. Natural Red 4)	H ₂ O ₂ , Carmines concentration, pH , time	D-optimal	Spectrophotometer	Bahadir & Rauf 2009
Toluidine blue (TB)	concentration, V ₂ O ₅ /TiO ₂ ratio	D-optimal	Spectrophotometer	Korbahti & Rauf 2008
Rose Bengal	Dye, pH, H ₂ O ₂	D-optimal	Spectrophotometer	Rauf et al. 2008
Remazol black	Dye, H ₂ O ₂ :Dye, H ₂ O ₂ :Fe ³⁺ ,Time	D-optimal	Spectrophotometer & COD	Hasan et al. 2012
Reactive azo dye Reactive Violet Reactive Yellow	Dyes, Type of oxidant, Fe ²⁺ , oxidant.	D-optimal d	Spectrophotometer & TOC	Grcic et al. 2010

Other applications of the RSM based on the D-optimal design in chromatographic techniques are applied to optimize analytical methods such as High-Performance Liquid Chromatography (HPLC), and gas chromatography-mass spectrometry (GC-MS). The D-optimal design has been extensively used as a famous RSM design for the optimization of process factors. Table 2.11 gives the different applications of the D-optimal design on chromatographic and fluorescence techniques for the optimization of process factors.

Recently, the D-optimal design has been broadly used in different applications especially in the pharmaceutical field due to the optimal selection of compounds using the analysis of data variance, which helps to develop a final model of the process (Arroyo et al. 2011). However, the enhancement of computational chemistry by the D-optimal design has been reported in previous studies (Brandmaier et al. 2012). The D-optimal design is also applied to the preparation of polymers to produce polymers with higher surface areas (Urban et al. 2010). However, last two years, the D-optimal design was intensively applied in food chemistry to optimize the preparation process for fatty acids from *Jatropha* oil and to increase the selectivity (Salimon et al. 2011). At same time, it has been reported recently that the best conditions for *Jatropha* oil hydrolysis via alkali catalysis and saponification can also be optimized using the D-optimal design (Salimon et al. 2012).

Table 2.11 Application of D-optimal design on in chromatographic and fluorescence techniques

Analytical instrument(s)	Analyte	Number of factor and runs	Reference
GC–MS	Metabolites	D-optimal (5 factors, 33 runs)	Jiye et al. 2005
GC–MS SPME	Non steroidal anti inflammatories	D-optimal (7/2, 1/4) 21 runs	Arroyo et al. 2011
GC–To FMS	Metabonomic compounds	D-optimal (3 factors, 10 runs)	Pan et al. 2010
HPLC	UV Test ionisable compounds	D-optimal and G-optimal designs on 5 factors	Torres et al. 2011
LC	UV Monolithic polymers as stationary phase	D-optimal (5 factors, 17 runs)	Urban et al. 2010
Size exclusion	Synthetic polymers	D-optimal (5/3, 30 runs)	Gruendling et al. 2009
CG- MS			
Fluorescence method	sulfadiazine determination in milk	D-optimal (3/3, 18)	Díez et al. 2007
Fluorescence spectroscopy	Sulfathiazole determination in milk	D-optimal (3/3, 18)	Morales et al. 2011
solid-phase extraction	sulfonamides determination in milk	D-optimal (4/3, 24)	Díez et al. 2010

CHAPTER III

MATERIALS AND METHOD

3.1 INTRODUCTION

The main aim of the present study is to optimize the process parameters in order to obtain a minimal size of ZnO NPs prepared by sol gel method. The most affective parameters such as molar ratio of starting materials, pH of solution and calcination temperatures were selected to optimize the synthesis process. The optimization of the process was achieved by response surface methodology (RSM), based on the D-Optimal design for lower runs of experiments. At the same time, to modify the optical properties and reduce the particle size, the doping process using some other metal ions was applied. To investigate the validity of the process, other metal oxides (semiconductors) were prepared under the same experiment conditions, as an economical way to scale up the process for certain applications.

The X-ray Diffraction (XRD), Field scanning Electron Microscopy (FSEM), Transmission Electron Microscope (TEM), Thermogravimetric-differential Scanning Calorimetry (TGA-DSC); and Ultraviolet–Visible (UV-Vis) spectroscopy were used to evaluate the structure, morphology and optical properties of ZnO NPs and metal oxides as photocatalysts. The photocatalytic degradation of chlorophenols as serious toxic compounds in waste water was employed to test the performance of ZnO and doped ZnO NPs. For the complete economical process, the photocatalytic degradation route was applied under direct solar radiation, which is environmentally friendly and a safe source of energy. Meanwhile, the High Performance Liquid Chromatography (HPLC), Gas Chromatography-mass spectroscopy (GC-MS), Ion Liquid

Chromatography (IC) and Chemical Oxygen Demand (COD) were employed to measure the efficiency of the photocatalytic degradation process, and determine the mechanism and intermediate compounds of chlorophenols after the degradation. Figure 3.1 indicates all procedures of the study from synthesis of ZnO and doped ZnO NP up to applications.

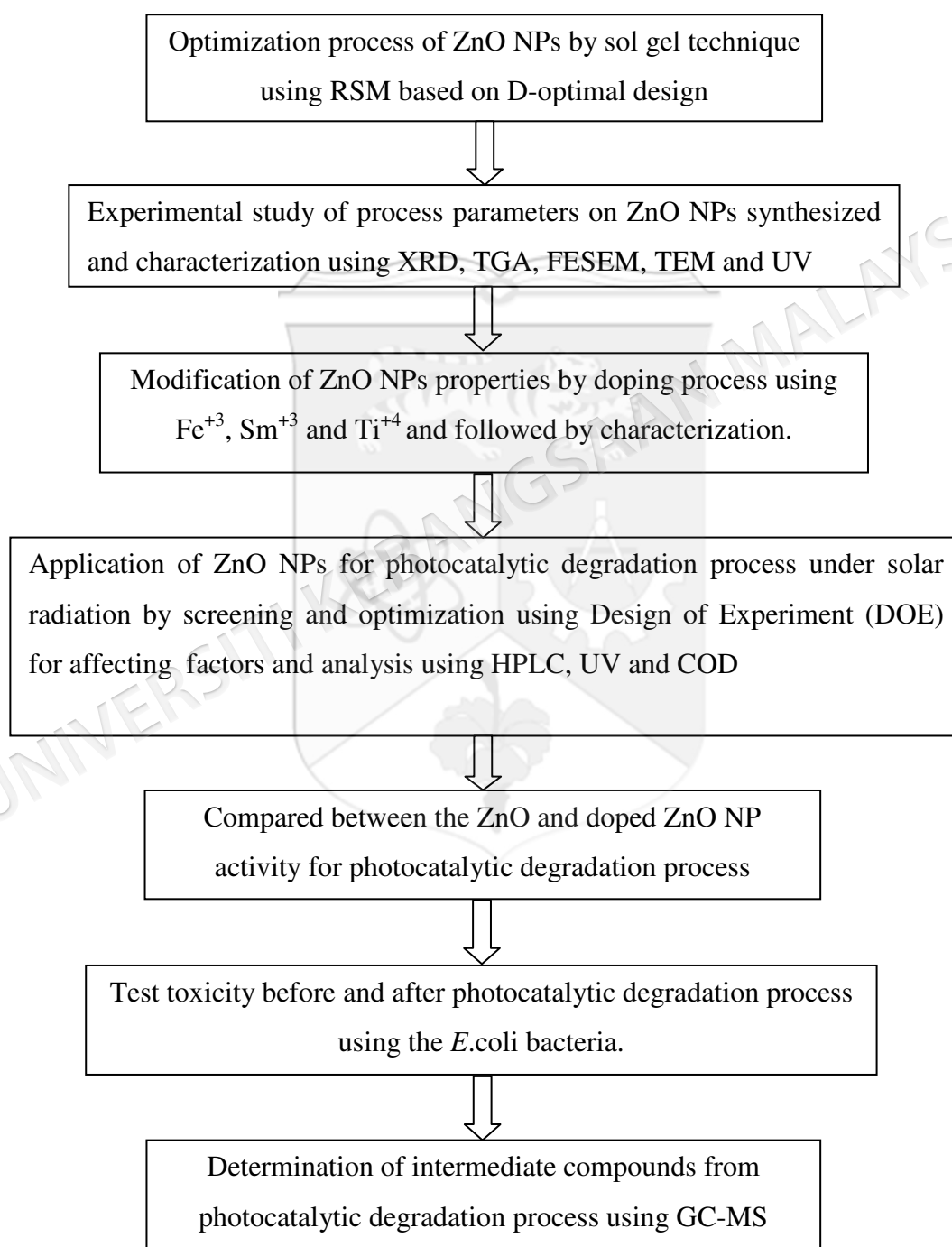


Figure 3.1 Shows the overall flow of study procedures

3.2 MATERIALS

To achieve the targeted objectives of this study, researchers need to choose suitable materials to produce the best results. This study involved two types of materials which the first are chemicals and solvents for the preparation of ZnO NP and other metal oxides nanoparticles; and the second, toxic compounds as the simulation pollutants used in this study.

3.2.1 Chemicals and Solvents

All chemicals and solvents with their specifications such as name, formula, molecular weight, purity and manufacturing company are listed in Appendix B. The data helps to prepare the smallest particle size of ZnO NP and other metal oxides under the control of process parameters. All required amount of chemical by mole was calculated based on the molecular weight while the balance as gram before being used in the preparation process. At the same time, the required amount of solvent was taken in volume (cm^3 , ml).

3.2.2 Degradant Compounds

All degradant compounds are divided into two groups, of which the first group is the toxic compound comprised of three chlorophenols (from Mono, Di and Tri) while the second, colour pollutants that include Methylene blue, Methyl orange and Methyl red, as shown in Appendix B.. The standards of chlorophenols compound under various concentrations were prepared. The calibration curves of these compound concentrations were established by using the High Performance Liquid Chromatography (HPLC). The specification and sample of the HPLC runs are shown in Appendix B.

3.3 PREPARATION METHOD OF ZnO AND DOPED ZnO NANOPARTICLES

The sol gel method is a wet-chemical route, which plays a main role in the nanostructure material field. This method has many promising properties such as cheap, and its low temperatures could produce higher activity of particles due to its smaller size and higher surface area. The sol gel technique is a suitable process to fabricate the metal oxide nanostructure with smaller sizes. The first step of preparation is sol, which is the source materials of ZnO NPs, as chemical solution in the liquid phase (solvent) and then produced into gel by integrating the network between the metal alkoxides. There are two steps to sol gel mechanism. The first is hydrolysis, and then followed by poly condensation reaction, to form the gel of metal oxide particles. At the drying stage of the gel at a low temperature ($\leq 80^{\circ}\text{C}$), the solvent is removed and it produces the porous material known as xerogel. Some parameters such as molar ratio of reactants ratio, pH and heat treatment have great influence on the size, shape, crystal structure and morphology, which in turn affect the quality of nano-materials. By controlling the physicochemical preparation parameters, one can synthesize size and particle shape upon application.

3.3.1 Preparation Procedures and Set-Up

The methodology of this study is to prepare ZnO NPs in smaller size via the sol gel technique. All experiments were carried out in batches of 500 ml of three-neck round bottom glass reactor. The procedures, which involved the optimization of process parameters as the first step of this study, were investigated.

Zinc acetate and oxalic acid dihydrate were used as starting materials. The ratio of zinc acetate to oxalic acid mixtures by mole ($Z_{ac}: O_{xa}$) were prepared in ethanol with varying molar ratios of 1:1, 1:2 and 1:3. The zinc acetate solution (90 ml of ethanol +10 ml of water) was heated in a water bath at $65\pm 5^{\circ}\text{C}$ under reflux condition for 30 minutes. At the same time, oxalic acid was mixed with 50 ml of ethanol in a beaker and stirred with a magnetic stirrer at $45\pm 5^{\circ}\text{C}$. The oxalic acid solution was then slowly added in drops to the zinc acetate solution under vigorous magnetic stirring to finally obtain a gel form. When the gel was completely formed,

the mixture was continuously stirred for an additional 60 minutes. All procedures of synthesis process were summarized in Figure 3.2.

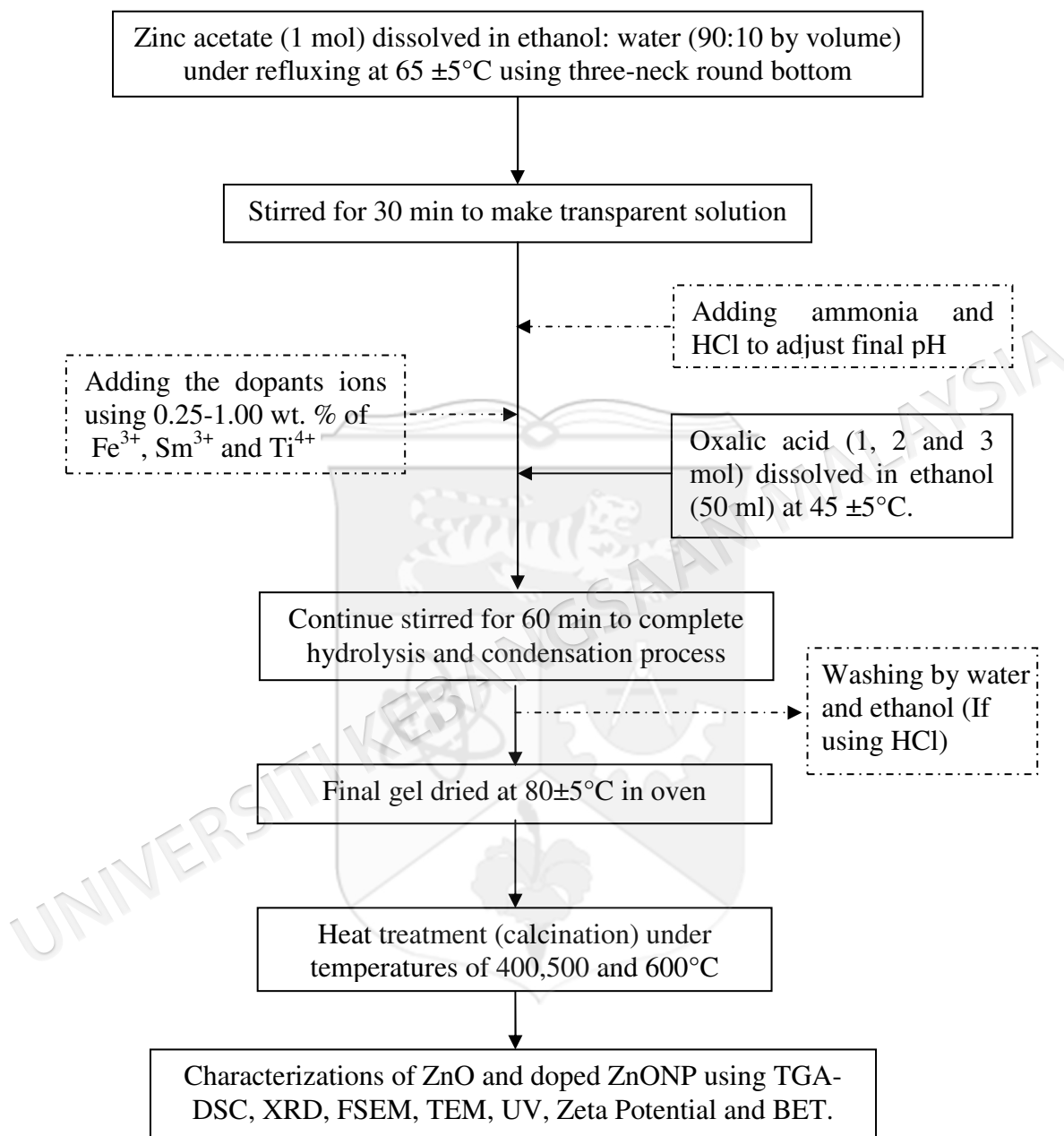


Figure 3.2 Experimental procedures of ZnO and doped ZnO NPs synthesized by sol gel method

The final pH of the reactant mixture was kept at 1.0, 3.0 and 5.0±0.2 by adding the required amount of hydrochloric acid and ammonia solution, respectively. The operating pH of 2.0±0.2 was obtained by the initial addition of oxalic acid to the zinc

acetate solution. The resulting gel was dried at $80\pm 5^{\circ}\text{C}$ to form the precursors for ZnO NPs (Xerogel) and portions of ZnO NPs were taken and thermally treated at calcination temperatures of 400°C , 500°C and 600°C for 2 hours.

3.3.2 Optimization of Process Parameters Using RSM

The process parameters of ZnO NPs synthesized by the sol gel method are needed to optimize for the minimum size of particle without adding any surfactants or capping agents. The optimization process selected has significant effect on ZnO size according to previous studies which the parameters such as pH, molar ratio and calcination temperatures showed direct effect on particle size (Dios et al. 2005; Alias et al. 2010). The Design Expert ® software (Stat Ease Inc., Statistic made easy, Minneapolis, MN USA, Version 6.0) is used for the optimization, as it saves material and time. The Response Surface Methodology (RSM) based on the D-optimal design is applied in order to obtain an empirical model for minimum size of ZnO particles. The D-optimal design is chosen for the lower runs of experiment to create the best model for response (particle size), as discussed in chapter II. The optimization of all parameters to produce the minimum size is investigated by crystal size using X-ray Diffraction (XRD) and then confirmed by the Transmission Electron Microscope (TEM).

3.3.3 Statistical Analysis of RSM

Statistical tools are able to explain the relationship between all factors of the preparation process (pH, molar ratio and calcination temperatures). The interaction between all factors needs to be analysed by statistical approaches and techniques. Several statistical approaches and techniques such as regression, response and lack fit are more effective analyses at this stage in the study.

Regression term is one of statistical techniques that can be used to explain the mathematical relationship between one independent variable (factors) with others known as regressors, as well as with the main dependent variables, known as response of the model that include controlled and noise variables. The coefficients of regression equation can be estimated by statistical technique, which determines whether it is

linear or non-linear. After the estimation of all parameters of the regression equation, the value of response would be estimated for each value given to the regressors.

A correlation analysis is a technique used to measure the linear association between response and regressors of the model. The correlation coefficient is divided into two types, as partial and multi, which determine the association between response with each and all regressors for the model. An important technique is the analysis of variance (ANOVA), which is one of the most powerful statistical techniques. ANOVA could identify the model's significant interaction between all factors of the process. The main objective to use Response Surface Methodology (RSM) in this study is to reduce the number of experiment runs in producing the minimum size of ZnO NPs. At the same time, RSM would optimize the parameters and characterization obtained by the model run in the lab. Figure 3.3 shows the optimization procedure of ZnO NPs synthesis by the sol gel process.

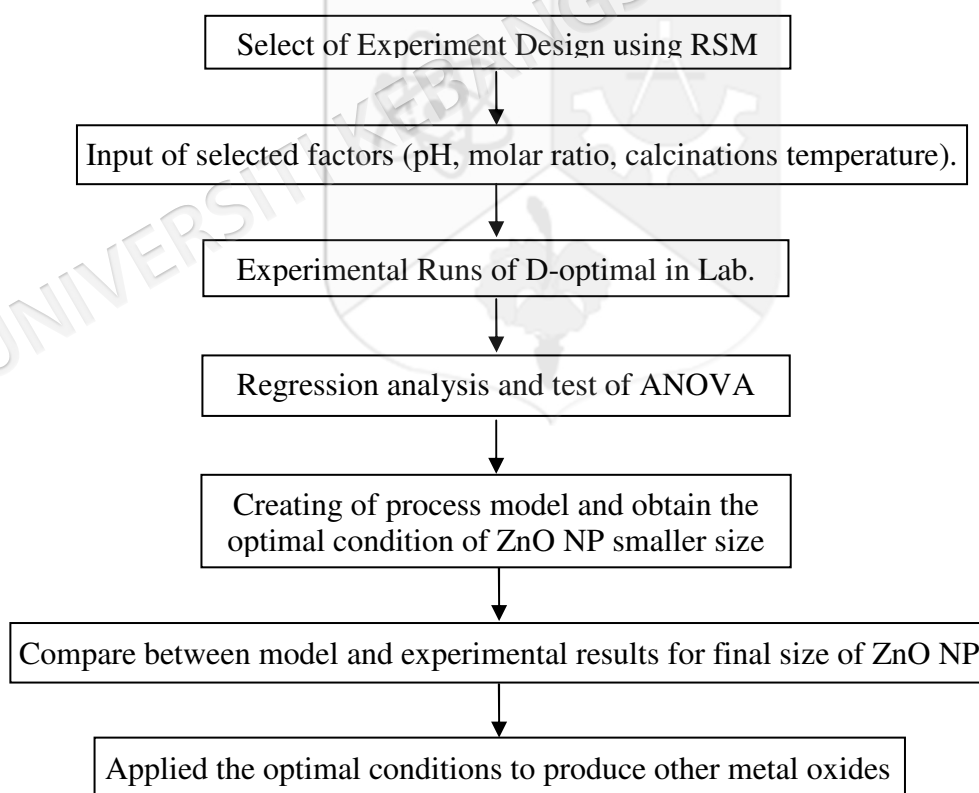


Figure 3.3 RSM procedures for optimization ZnO NP synthesis process

A. RSM Based on D-Optimal Design

The optimization of all parameters for minimizing the size of ZnO NPs is carried out by RSM, based on the D-optimal design. This optimization is conducted to evaluate the effects of all variables on the response. The D-optimal design offers lower experimental runs for the same number of factors compared with the central composite design. Besides reducing experimental runs that results in low in cost it offers good interactions between the factors. This design is able to produce optimal conditions of experimental, avoiding any problem within the optimization process (Myers & Montgomery 2002). The criterion of the D-optimal design includes choosing the points of mixture design in a constrained region. Design points were selected by criterion from the list candidate points so that minimum variances of the model regression coefficients are created. The setting of candidate points used is dependent on the order of the experiment model, desired to fit (Korbahti & Rauf 2008).

B. Factors and Experimental Runs Based on D-optimal Design

All independent variable factors and their respective levels used to determine the optimum condition for minimum size of ZnO particles (Y, response) are summarised in Table 3.1. The three significant factors in this study for model design include molar ratio of starting materials of zinc acetate to oxalic acid (mol Z_{AC} : mol OX_{AC}), pH of solution and calcination temperatures. The average crystal size of particles and structure of the resulting ZnO NPs were analysed by X-ray Diffraction (XRD). The size of ZnO NPs was evaluated by the Transmission Electron Microscope (TEM).

Table 3.1 Parameters and levels of D-optimal design

Independent variables	Factor levels			
	X_i	-1	0	+1
Molar ratio	X_1	1	2	3
PH	X_2	1	3	5
Calcination Temperature ($^{\circ}C$)	X_3	400	500	600

In order to determine the effects of the independent variables on the size of the resulting nanoparticles, a D-optimal design consisting of 18 runs were carried out. The results of these experimental runs are presented in Table 3.2 together with the respective experimental conditions. The independent variables X_1 , X_2 and X_3 , represent the molar ratio (mol Z_{AC} : mol OX_{AC}), pH and calcination temperature ($^{\circ}C$), respectively. The low and high values as indicated in Table 3.1 were used to determine all the independent variables. The linear or quadratic model of the optimisation process is used to explain the relationship between the given factors as indicated in Equation (3.1).

$$y = \beta_0 + \sum_{i=1}^k \beta_i \chi_i + \sum_{i=1}^k \beta_{ii} \chi_i^2 + \sum_{1 \leq i < j \leq k} \beta_{ij} \chi_i \chi_j + \varepsilon \quad (3.1)$$

where, β_{ii} is coefficients of the quadratic terms. To evaluate all parameters, the design of experiment should run at least three factor levels (Gilmour 2006).

Table 3.2 Experimental runs of D-optimal design

Std	Run No.	Molar ratio (X_1)	pH (X_2)	Calcination Temperature ($^{\circ}C$) (X_3)
1	12	3	5	400
2	8	3	5	600
3	17	1	5	600
4	7	3	1	600
5	11	1	1	500
6	9	2	5	500
7	13	2	3	600
8	3	3	3	500
9	2	3	1	400
10	16	1	3	400
11	6	2	2	450
12	4	1	1	400
13	15	1	5	400
14	5	1	1	600
15	10	1	5	600
16	14	3	51	400
17	18	3	1	600
18	1	3	5	600

By using Eq. (3.1), the crystal size of ZnO NPs was evaluated with the magnitude of the interaction between the independent variables and the response was obtained via the ANOVA statistical technique. The correlation of fit for the polynomial model was expressed using the values from the normal regression (R^2) and the adjusted regression (R^2_{adj}) coefficients.

One of the important commercialize factors is to enable this optimization to synthesize other metal oxide such as TiO_2 , $\alpha-Fe_2O_3$, NiO, CuO and Co_3O_4 by using the sol gel method under the same optimal conditions. To investigate the crystal and particle sizes, the X-ray Diffraction (XRD) and Transmission Electron Microscope (TEM) were used for all metal oxides.

3.4 DOPING OF ZnO NANOPARTICLES BY DIFFERENT METAL IONS

The ZnO NPs have limited activity for photocatalytic degradation of organic pollutants especially when used under solar radiation. The limitation of absorbance under visible region indicates the limitation, of which it requires enhancement of ZnO NP for better performance. The application of solar in countries with sufficient quantity has made it easy and economical for photocatalysis process. Solar spectrum consisting of 43-46% visibility and 4-5% ultraviolet light is free, environmental friendly and is a renewable source of energy. The limiting recombination of the photo generated electrons and holes are one of the effect control factors on photocatalytic efficiency of semiconductors, which is a challenge to shift the absorbance to visible light region or increase the surface area that is exposed to pollutants (Paola et al. 2011). Improvement of the properties by dopants to the semiconductor has been reported in the last decade. The doping processes with noble metal such as Pt and Au have shown higher effectiveness in enhancing photocatalysts process. These metals are expensive and many studies have been conducted to search for other lower cost metals that also improve the performance process. In the last decade, metal transition and rare-earth ions have been used as semiconductors to enhance the photocatalytic degradation activity (Vijayana et al. 2009; Zhou et al. 2006).

The transition metal ions such as Ti^{4+} (Liu et al. 2005), Ni^{2+} (Liu et al. 2008) and Fe^{3+} (Debernardi et al. 2007) have been used as dopants of ZnO thin films to improve the optical properties while others studies showed ferromagnetic properties of doped ZnO NPs (Liu et al. 2008). Doping of semiconductors by metal ions has been found to be the best way to improve the activity under visible light (Kim et al. 2005). Moreover, the optimum of doped-metal concentration is one of the important factors on photocatalytic activity. Generally, more concentration than optimal increases electron-hole recombination and leads to a decrease in activity.

There have been no recent studies on dopant of different ions such as Fe^{3+} , Sm^{3+} and Ti^{4+} on ZnO NP and their performance in photocatalytic degradation of chlorophenols under direct solar light. For this reason, these metal ions are selected as typical ions to improve the ZnO NPs activity for photocatalysts process. To achieve part of this study's objective, a lower concentration of dopant ions is employed, including 0.0, 0.25, 0.5, 0.75 and 1.00 wt %.

After optimization process of all parameters using RSM based on the D-Optimal design, optimal values of molar ratio, pH and calcination temperature were used. To prepare doped ZnO samples, pure ZnO NP with dopant ions were added to the zinc acetate solution under vigorous magnetic stirring, followed by the adding of oxalic acid solution. The final gel of doped ZnO NP was dried at $80 \pm 5^\circ\text{C}$ to remove the solvent and then calcined at 400°C for 2 hours. These procedures were repeated for all dopant types but in different concentrations (wt %). To investigate any improvement of ZnO NP after doping, a series of analysis using XRD, TGA-DSC, FSEM, TEM and UV-Vis measurements were applied.

3.5 CHARACTERIZATION OF ZnO AND DOPED ZnO NANOPARTICLES

After the optimization of process parameters to synthesis of ZnO NPs by sol gel method under different conditions, characterizations and analysis were conducted to determine the effects of different parameters on structure, particle size, optical properties and morphology of ZnO NPs. Each characterization displayed different properties of each ZnO NP sample under different experimental conditions.

The thermal stability of ZnO NP precursors was analysed by the Thermogravimetric-Differential Scanning Calorimetry (TGA-DSC). To determine crystal size and structure phase of ZnO NP, the X-ray Diffractometer (XRD) was used. The surface morphology was viewed using the Field Emission Scanning Electron Microscope (FESEM) while the particle size by Transmission Electron Microscope (TEM). The optical properties based on absorbance were measured by UV/Vis spectrophotometer. All of these characterisations were run at room temperature. All of these parameters were applied to doped ZnO NP to investigate the successful doping process by different ions. On the other hand, all characterizations were applied to evaluate the sole gel method under optimal conditions for other metal oxides production. All of these characterizations were described individually, including the model with company of instrument and all specific conditions of measurement.

3.5.1 Thermal Analysis

The oxidation temperature of organo-Zn and its doping with other metal were determined by the Thermal Gravimetric Analysis and Differential Scanning Calorimetry (TGA-DSC) instrument, model STA 449F3, Jupiter, NETZSCH, Germany. The TGA-DSC is suitable for thermal study and thermal behaviour of materials. The fast heating of the samples was incurred by the furnace, which has an extremely accurate temperature control. Certain amount of material (about 10-15 mg) was placed in open pan samples (alumina) to ensure the bottom of the pan receives good thermal contact. The same material of pan is used for the sample and reference in the testing. A heating rate of 10°C/min from room temperature to 800°C was carried out. The final graph measured the percentage of weight loss according to the temperature range within the heating profile of the samples.

3.5.2 X-Ray Diffraction Analysis

The structure and crystallite size of ZnO, doped ZnO NPs and other metal oxides were identified using the X-ray Diffractometer, model D8 Advance Bruker AXS X-ray, Germany with Cu K α radiation of 1.5406 Å. All powder samples were papered in a rotary surround plate, which covered the hall bottom place with powder. All samples

were scanned from 20 to 80° of 2θ at a rate of 0.2 degree/second. The crystallite size, D was calculated based on the Scherrer equation below (Cullity & Stock, 2001):

$$D = \frac{K \lambda}{\beta \cos \theta} \quad (3.2)$$

where K is the Scherrer constant (K=0.89), λ is the X-ray wavelength, β is the peak width of half maximum, and θ is the Bragg diffraction angle. To evaluate the structure and lattice strain of samples, the EVA software (version 2) was used. The XRD patterns of all samples were compared with the Joint Committee on Powder Diffraction Standards (JCPDS), which is a standard from the software library.

3.5.3 Field Emission Scanning Electron Microscope

The morphology of ZnO and doped ZnO NPs were investigated and viewed using the Field Emission Scanning Electron Microscope (FESEM) model SUPRA 55VP. The aim for using FESEM is to get clear and less electrostatically distorted images of surface sample, which are better than conventional SEM. FESEM, could determine the size of nanoparticles with higher resolution and low charging of sample surface. The elements distribution of the sample were evaluated by combining the FESEM with Energy Dispersive X-ray analysis System (EDX), model OXFORD INCA Penta FETx3. All samples were coated with gold using the Bio Rad microscience division SC 500 to prevent or reduce electrical charging during testing. The magnification of morphology observations was in the range of 100 and 150 k to get clearer images.

3.5.4 Transmission Electron Microscope

The real size of ZnO, doped ZnO NPs and other metal oxides were determined using a Transmission Electron Microscope (TEM), Philips CM200, model JEOLJEM 2100, Netherland. The TEM was operated at 200kV as the voltage acceleration. Ethanol was used as solvent for all specimens and prepared by adding small amount of particles and then allowed for more disperse under ultrasonic for 10 minutes. One drop of suspension solution was induced to copper grid to evaporate the ethanol under air

before imaging. The Olympus BX51 microscope equipped with an MP5Mc/OL digital camera was used to take the images under different magnifications.

3.5.5 Brunauer-Emmett-Teller (BET) Surface Area

The Brunauer-Emmett-Teller (BET) surface area of ZnO and doped ZnO NPs were estimated by nitrogen adsorption in Micromeritics ASAP 2020 Accelerated Surface Area and Porosimetry System, USA. The surface area (BET) was obtained from adsorption data in the range of 0.05-0.3 for (P/P_0) relative pressure. The total adsorption of nitrogen was used to determine the volume and average size of pore. The average pore size was found from desorption isotherm by using the Barrett-Joyner-Halenda (BJH) method (Sing, et al. 1985). A 0.1 to 0.3 gram of sample was degassed under nitrogen at 350°C for some hours to remove any water or humidity from sample and then the analysis started.

3.5.6 Zeta Potential (Surface Charge)

The surface charge of ZnO and doped ZnO NPs were measured using the Zeta Sizer, model Nano-ZS, Malvern instruments Inc. (UK). This property is very important for the estimation of activity of all the catalysts in the application. Moreover, the change of the surface plays the main role in the adsorption process within the application. Knowing the type of charge (positive or negative) of the catalyst surface, based on the pH medium, helps to determine which pH is suitable to achieve maximum efficiency of the catalyst. The surface charge results would reflect the behaviour of the catalyst surface within the application process, hence could avoid any pH that reduces efficiency. To measure the surface charge of any sample, about 0.01 w/v (weight of sample / volume of water) was used under several pH medium. 1.0 M of sodium hydroxide and 1.0 M of hydrochloric acid were used to adjust the desired pH from 4.0 to 11.0. For equilibrium of the solution, the sample was left for about 60 minutes before it was sent for analysis. The capillary cell with minimum volume 0.75 ml of sample was used for analysis.

3.5.7 Diffuse Reflectance using UV/Vis Spectrophotometer

Diffuse reflectance spectra of ZnO and doped ZnO NPs were recorded by the UV/Vis spectrophotometer, Perkin Elmer, model lambda 35, USA to determine the band gap. The spectra were recorded at room temperature with the wavelength ranging from 200–800 nm. The scans of spectrophotometer were collected in slow speed mode for all samples. The halogen lamp and deuterium lamp at 390 nm was supplied as light source. The baseline correction was performed using a calibrated sample of barium sulphate (BaSO_4) as a standard. The liquid sample also runs to determine the wavelength absorbance of pollutants and efficiency in removing colour pollutants. The samples were run with slow speed at 0.2 nm intervals and 0.5 nm as slit width. One set of quartz cells with 5 ml volume was used to perform all experiment runs. The deionized water was used as blank solution with all the samples.

3.5.8 Atomic Absorption Spectrometer

The zinc ions (Zn^{2+}) concentration in water solution before and after degradation process was detected by using the Perkin Elmer, model A Analyst 800, (USA). A 10 ml of solution after the ZnO particles were filtered was sent to atomic absorption spectrometer to determine the zinc ions content according to the standard. The Zn^{2+} standard was supplied by BDH Prolabo Chemicals Company with concentration of 1000 ± 5 mg/l. Deionized water ($18 \Omega \cdot \text{cm}$) was used as a blank for Zn^{2+} content. The calibration of the atomic absorption spectrometer instrument for Zn^{2+} concentration was performed with the standard and then compared to the sample after degradation process. Additionally, Zn^{2+} concentration was determined for doped ZnO samples (by Fe^{+3} , Sm^{+3} and Ti^{+4}) and compared to undoped sample after the degradation process. The Electrodeless Discharge Lamp (EDL) was the main source used for atomic absorption.

3.6 APPLICATION OF ZnO NANOPARTICLES FOR CHLOROPHENOLS DEGRADATION UNDER DIRECT SOLAR RADIATION

The activity of ZnO and doped ZnO NPs by metal transition and other metal oxides were evaluated to determine the degradation of toxic pollutants. Chlorophenols were

used in this study to represent a serious environmental pollutant. Different pollutants were also used to test the performance of ZnO NP, including colour pollutants (Methylene blue, orange, red and lignin). Effects of some parameters on the photocatalytic degradation efficiency such as loading of ZnO catalyst, calcination temperature of ZnO, pH of solution, initial concentration of chlorophenols and intensity of solar light were investigated. All of these parameters were optimized using DOE-based RSM to determine the most significant parameter for the degradation of these compounds, following which, the validation result from the model was compared with the experimental. Additionally, the effects of different ions Fe^{3+} , Sm^{3+} and Ti^{4+} doped ZnO NP with various concentrations from 0.0 to 1.0 wt. % were also tested on their degradation efficiency. All these experiments for degradation comparison between ZnO and doped ZnO NPs were carried out in the same procedures and conditions for optimization.

3.6.1 Standard of Degradant Compounds

All standards of the chlorophenols were prepared by dissolving different concentrations in the deionized water. The standard of 2-chlorophenol (2-CP), 2,4-dichlorophenol (2,4-DCP) and 2,4,6-trichlorophenol (2,4,6-TCP) were prepared in the volume of 1 to 150 mg in a bottle of one litre volume. Chlorophenols standard calibration curves were determined using the HPLC (Agilent 1200) with UV detector at 254, 284, 293 nm for 2-CP, 2,4-DCP and 2,4,6-TCP, respectively as shown in Appendix C. Additionally, methylene blue, methyl orange, methyl red and lignin were prepared in the volume of 100 to 6.25 mg/l. The colour compounds were analysed using the UV/Vis spectrophotometer (Perkin Elmer, lambda 35) with wavelength between 200 to 800 nm. The absorption peak (λ_{max}) of Methylene blue, orange, red and lignin was determined at 665, 450, 460 and 520 nm respectively.

3.6.2 Experimental Set Up for Solar Photocatalytic Degradation Process

Photocatalytic degradation process was carried out in a cylinder batch reactor (non-concentrating type slurry reactor) with dimension of (D=6.5 cm and h=3.8 cm) as shown in Figure 3.4. A 125 ml of the reactor is used to run all of the experiments, in which each volume of 100 ml was used. The area of reactor, which was exposed to

solar light, was 144 cm^2 . The degradation process was conducted by using 100 ml of any chlorophenol solution with different concentrations of 50 to 150 mg/l. To reach the adsorption-desorption equilibrium, the optimum amount of ZnO (2g/l) and doped ZnO NPs (1g/l) were added to the solution and stirred under dark for 60 minutes. The adsorbed of chlorophenol on ZnO surface was determined. Then the solution was exposed to solar light for photoreaction to take place. A 0.5 to 1.0 ml was withdrawn in a 15 minute interval, centrifuged and then filtered. To determine the non degraded chlorophenols concentration, High-performance Liquid Chromatography (Agilent 1200 HPLC) was employed. The toxicity of chlorophenols before and after degradation was evaluated using *E.coli* according to inhibition zone of growth around the paper disk. All experiments were run under optimum solar intensity, which was investigated by Skye lynx type SDL 5100, and placed very close to the photo reactor to record solar intensity.



Figure 3.4 Batch solar photoreactor (non-concentrating type slurry reactor)

3.6.3 Effects of Experimental Parameters using RSM design

Generally, to optimize the photocatalytic degradation of chlorophenols, the first step is to identify all affective factors in the process as reported earlier (Sakkas et al. 2010). Recently, statistical design has been applied to wide photocatalytic application to minimize the cost and time and improve the process for scale up in the future (Sakkas et al. 2010). To control the degradation process in this study, affecting of factors are selected, such as the pH of solution, solar intensity, calcination temperatures of ZnO,

loading of ZnO and initial concentration of chlorophenols. This study needs to determine the effect of independent variables using screening test as a good way to choose the most significant factors from overall factors. The two-level full fractional design is a famous design to identify the significant factors in studies of method of screening test (Box et al. 2005). All factors with their levels, summarised in Table 3.3, were screened to identify the significant factors of the photocatalytic degradation process.

Table 3.3 Parameters and their levels of two level full fractional design

Independent variables	Factor levels		
	X_i	-1	+1
PH	X_1	4	8
ZnO loading (g/l)	X_2	1	3
Calcination Temperature ($^{\circ}\text{C}$)	X_3	400	600
Solar intensity (W/m^2)	X_4	10	20
Initial concentration (mg/l)	X_5	50	150

A 16 experimental runs were created to identify the significant factors of the process, as shown in Table 3.4. All experiments were carried out using 100 ml of 2-CP as example of chlorophenols with different concentrations. The catalyst with aqueous solution of 2-CP were stirred for 60 minutes under dark to allow equilibrium to be achieved, and then it went under irradiation time for another 60 minutes to determine the degradation efficiency of the process (DE, %) and removal of Chemical Oxygen Demand (COD) as a target responses.

After the screening, the optimization of process is required using the RSM. RSM is an excellent technique, most used for analysing problems when the response is influenced by factors, to create the optimized conditions for response (Montgomer, et al. 1991). At the same time, RSM is an efficient technique to apply for wide chemical reactions in industrial processes to create a high quality of product or allow the process to be more economical for application.

Table 3.4 Experimental runs of screening using two –level full fractional design

Std	Run No.	X ₁	X ₂	X ₃	X ₄	X ₅
1	4	4	1	400	10	150
2	7	8	1	400	10	50
3	1	4	3	400	10	50
4	6	8	3	400	10	150
5	14	4	1	600	10	50
6	8	8	1	600	10	150
7	11	4	3	600	10	150
8	3	8	3	600	10	50
9	2	4	1	400	20	50
10	13	8	1	400	20	150
11	9	4	3	400	20	150
12	12	8	3	400	20	50
13	10	4	1	600	20	150
14	5	8	1	600	20	50
15	16	4	3	600	20	50
16	15	8	3	600	20	150

After applying a screening test of all the selected factors, the RSM was required to determine the optimal conditions of photocatalytic degradation process using the most significant factors, which are given in Table 3.5. The D-optimal design was used as RSM design for optimization of different application process, which have been reported recently (Brandmaier et al. 2012b; Salimon et al. 2012a).

Table 3.5 Parameters and levels for photocatalytic degradation process

Independent variables	Factor levels			
	X _i	-1	0	+1
PH	X ₁	4	6	8
Calcination Temperature (°C)	X ₂	400	500	600
Solar intensity (W/m ²)	X ₃	10	15	20

An 18 runs of experiments were generated by the D-optimal matrix design as summarised in Table 3.6. The model fitting was employed by Design-Expert software (version 6.0, Stat-Ease, Inc.) to produce the best fit of model. The degradation efficiency of the process (Y, %) and removal of Chemical Oxygen Demand (COD) were used as final responses.

Table 3.6 Experimental runs of optimization using D-optimal design

Std	Run No.	pH (X ₁)	Calcination Temperature (X ₂)	Solar intensity (X ₃)
1	14	4	400	10
2	11	8	400	20
3	15	4	400	20
4	18	8	600	20
5	7	6	600	10
6	9	6	400	15
7	6	8	500	15
8	13	6	500	20
9	5	8	400	10
10	1	4	600	15
11	17	5	500	15
12	10	4	600	10
13	16	8	600	10
14	12	4	600	20
15	4	8	600	20
16	3	4	400	20
17	8	8	400	10
18	2	8	400	20

3.6.4 Location of Experiments

All experiments of degradation process were conducted in the Faculty of Engineering & Built Environment, Universiti Kebangsaan Malaysia (UKM) with GPS location latitude of 2°, 55', 23'' N, longitude 101°, 46', 23'' E and altitude 35.64 m. The experiments' location, GPS coordinates and sunny day images are shown in Figure 3.5. This location was selected in the faculty because the experiment and analysis laboratories are close to each other, giving no delay in time to achieve all analysis.

3.7 EXPERIMENTAL ANALYSIS

After all the experiments of photocatalytic degradation process are run under the different conditions, several analyses were carried out to determine the performance of the process. All required analysis such as High-performance Liquid Chromatography (HPLC), Ion Liquid Chromatography (IC), Gas Chromatography–Mass Spectrometry (GC-MS); Chemical Oxygen Demand (COD) and toxicity test are described below with specification of each instrument.

3.7.1 High-Performance Liquid Chromatography

High-performance Liquid Chromatography (HPLC), Agilent technologies model 1200 series equipped with column of Jones chromatography SEA SDN BHD was used. The Genesis C18 Colum with dimension of 250 mm x 4.6 mm x 4 μ m and a variable wavelength UV detector was employed to measure the concentration of chlorophenols before and after the degradation process. An acetonitrile: water solution (20:80 v/v) and 0.01 M phosphoric acid (H_3PO_4) as the mobile phase with a flow rate of 1.0 ml/min were applied. The injection volume of 20 μ l and chlorophenols were detected at a wavelength of 254, 284, 293nm for 2-CP, 2,4-DCP, 2,4,6-TCP respectively. The photocatalytic degradation efficiency (DE %) was calculated using equation below:

$$DE \% = \frac{C_0 - C}{C_0} \times 100 \quad (3.3)$$

where C_0 is the initial concentration at $t = 0$ and C is the concentration of chlorophenols at different intervals of irradiation time, $t = t_{\min}$.

3.7.2 Ion Liquid Chromatography

The anions and cations releases before and after the degradation process of the chlorophenols were measured by the Ion Liquid Chromatography (IC). Ion Liquid Chromatography was used to detect Cl^- (anion) by using a conductivity detector (882 compact IC plus) with a column type Metrosep A Supp 5 150/4 and with the solution $\text{CO}_3^{2-}/\text{HCO}_3^-$ (3.2/1 mM) as the eluent. Standard anions and cations were supplied by Merck Company with concentration of 1000 ± 5 mg/l. The calibration of instrument performance was tested using deionized water (UP, 18 Ω .cm), which is free of anions and cations. All samples before or after degradation were diluted by water up to hundred times and 10 ml of each sample were subjected to Cl^- determination.

3.7.3 Gas Chromatography

The intermediates compounds within degradation of chlorophenols were identified using the Gas Chromatography–Mass Spectrometry (GC-MS), Agilent technologies model 7890A-GC system. During the degradation process, the intermediates were

measured by taking 5 ml of the solution after certain time of solar exposure, separating the ZnO NPs and then put in a 10 ml screw-capped sample tube. The sample was adjusted to pH of 9.0 by adding solution of NaOH. Mix 0.5 ml of acetone and 0.5 ml of n-hexane with excess amount of 100 μ l of acetic anhydride and then add previous sample in test tube in order to extract chlorophenol fragments (Al-Janabi, et al. 2012). Final mixture was shaken vigorously by vortex for 10 minutes and then followed by separation through centrifuge at 6000 rpm for 5 minutes. The organic layer containing n-hexane with intermediates (acetylated product) was collected and then injected to GC-MS. The GC-MS runs with column of HP-5 with dimension 30m x 320 μ m x 0.25 μ m. The operation conduction, including of oven temperature started at 60°C for one minute, and then raised by 20°C/min up to 300°C with the injection volume of sample at 1 μ L. The total time for the run of sample amounted to about 21 minutes and helium gas was used as carrier.

3.7.4 Chemical Oxygen Demand

The photocatalytic degradation process was evaluated by the Chemical Oxygen Demand (COD) removal, which indicates the oxygen consumed per litre of sample solution before and after treatment. The COD tests were carried out according to close reflux, colorimetric method (APHA, 1989), using HACH DR/2010 Spectrophotometer with COD reactor. A 2 ml of solution sample before and after treatment was added to low range (LR= 0-150 mg/l) or high range (HR=150-1500 mg/l) of reagent consists of potassium dichromate solution ($K_2Cr_2O_7$) supplied by HACH company, USA. Before measuring the COD, the final solution was heated at 150°C in a digestion reactor for 2 hours and was cool down at room temperature. The chlorophenols reacts with $K_2Cr_2O_7$, of which oxidation of dichromate (Cr^{2+}) to chromic ion (Cr^{3+}) is detected by the changes of colour according to the concentration. Following this reaction, COD of the sample was measured by spectroscopic, according to the concentration of Cr^{3+} produced from the reaction at absorbance wavelength of 420 and 620 nm for LR and HR respectively. The COD % of removal was calculated using Equation below:

$$COD \% = \frac{COD_0 - COD}{COD_0} \times 100 \quad (3.4)$$

where COD_0 is before degradation at $t = 0$ and COD is after degradation of chlorophenols at different intervals of irradiation time, $t = t_{min}$.

3.7.5 Toxicity Evaluation

To evaluate the chlorophenols toxicity before and after degradation, *E.coli* bacteria were applied with strain of ATCC 777, as shown in Appendix D. The toxicity test was selected as an indicator for photocatalytic degradation of toxic material supporting solar detoxification in this study. The medium of *E.coli* bacteria's growth was prepared through 13 g/l concentration nutrient broth (Oxoid Company) in distilled water. One colony of *E.coli* bacteria was used to grow it in 10 ml medium and was left for 24 hours under aerobic condition growth incubation at 37°C with shaking at 150 rpm. For plate test disk, nutrient agar (Oxoid Company) with concentration of 28 g/l was used.

All medium were sterilized by autoclaving at 121°C for 20 minutes before use. To prepare agar plates, approximately 15 ml of nutrient agar was placed in a plastic petri dish. The plates of agar were solidified under room temperature before being used to adsorb the liquid containing chlorophenols before and after degradation. A 10^7 CFU (colony formed unit) of culture was transferred to the petri dish containing nutrient agar and distributed by L-loop. It was left for 30 to 60 minutes before the toxicity test was considered (Kayalvizhi & Gunasekaran 2010). The sterilized paper disc was placed on the surface agar, followed by 10 μ l of chlorophenols before and after degradation at certain time, with one of control (distilled water) injected to the surface of the paper. The petri dishes were incubated at 37°C for 24 hours and then measured for toxicity. The toxicity evaluation by inhibition growth of the *E.coli* bacteria was estimated based on the clear zone on each of the paper disc as shown in Figure 3.5.

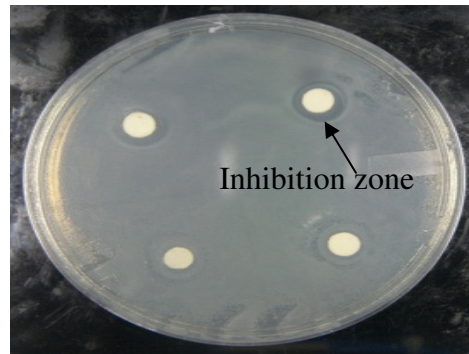


Figure 3.5 Inhibition zone determination of *E.coli* bacteria's growth

3.8 SOLAR INTENSITY MEASUREMENTS

The UV solar intensity was measured using a Skye lynx type SDL 5100, which consists of two sensors of UVA and UVB (Skye instruments Ltd, UK) as shown in Figure 3.6 (a). Dimension of each sensor is 69 mm high and 34 mm diameter with detector of GaAsp photodiode and Gap photodiode for UVA and UVB respectively (Appendix E). The working range of 0-100 W/m² for UVA under spectral response between 315-380 nm and 0-5 W/m² between 280-315 nm for UVB with operating temperature of -30°C to +60°C. All data of intensity was stored by DataHog logger with large memory and extended battery life to allow long term projects to be monitored at remote sites. The dimension of Data Hog is 122 mm length x 120 mm width x 105 mm highest while the operating temperatures ranged between -20°C and +70°C.

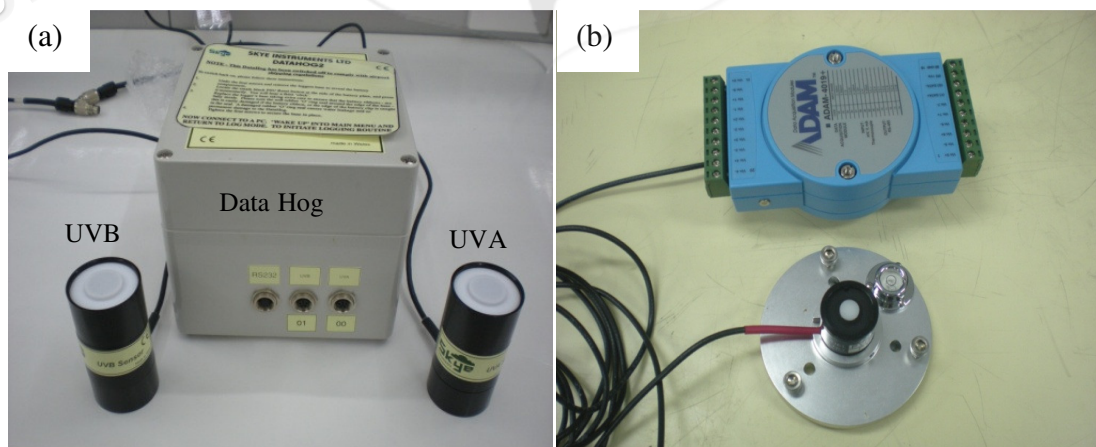


Figure 3.6 (a) Solar intensity measurements set up, and (b) Radiometer for determination of total solar radiation.

The UV intensity of solar radiation was recorded for all experiments under similar conditions, including sunny, semi-cloudy and cloudy days. The intensity was measured every 5 minutes and found to be nearly constant over the entirety of the experimental period. To collect recording data, the software version 2005 with serial no of 7368 was used.

The total solar radiation including the UV, visible and infrared was measured for sunny, semi-cloudy and cloudy days by the radiometer in Solar Energy Institute (SERI) in UKM. Figure 3.6 (b) showed the radiometer instrument for solar radiation recording with data logger. The radiometer consists of sensor for recording the solar radiation type of Pyranometer No.PY 5812(Hukseflux thermal sensors, USA). The range of wavelength can be measured between 370 nm and 1140 nm with accuracy of $\pm 5\%$ and range of irradiance between the 0 to 1100 W/m². The Pyranometer dimension is 2.4 cm in diameter; 2.75 cm high and the material is anodized aluminium with case acrylic lens. ADAM-4019 data logger consisted of eight differential channels for individual input type, such as thermocouple (mV) with input impedance of 20 M Ω . Some of the specifications include operating temperature between -10~70° C (14~158° F), humidity of 5 - 95% RH, resists over-voltage of up to 35 V and accuracy of measurement of about $\pm 0.1\%$ of voltage input.

CHAPTER IV

SYNTHESIS OF ZnO NP AND ITS CHARACTERIZATIONS

4.1 INTRODUCTION

Recently, the sol gel method has become an alternative technique for the synthesis of ZnO NP at a lower cost in order to control the size and morphology of the particles (Babu et al. 2013). Generally, many parameters which influence the particle size and properties of ZnO, such as the solvent, starting material, additive chemicals (capping agent or surfactant), pH of the media and concentration of the materials, have been reported (Masuda et al. 2007). The main focus of this work is to control the size of ZnO NP through the molar ratio (concentration of the starting materials), pH of the solution and the calcination temperature, without using any chemical additives. The molar ratio of the starting material is considered to be one of the parameters which has a greater effect on the size and shape of the ZnO NP (Dios et al. 2005). Moreover, it has been reported earlier that the pH of the solution also influences the size and shape of the ZnO NP (Alias et al. 2009). Additionally, the type of solvent also affects the size and shape of the ZnO NP. An organic solvent, such as ethanol, has been observed to be the best for producing smaller-sized and uniform, spherical-shaped particles (Zhang et al. 2002).

4.2 OPTIMIZATION OF ZnO NP

To achieve the objective of this study, the design of experiment (DOE) based on the Response Surface Methodology (RSM) has been applied as a statistical technique. The RSM has been indicated to be a good technique for studying the effects of synthesis parameters (factors) on the target (response) and for the building of experimental

models with interactive parameters (Karacan et al. 2007). One of the advantages of the RSM is the evaluation of the interactive effects between factors that are selected as well as the reduction in the number of experimental runs and the time taken within the optimization of the process compared to the classical process (Ismail et al. 2005). For this proposal, the famous D-optimal design for the lowest number of experimental runs with good interactions using three factors have been reported for many applications over the last two years (Arroyo et al. 2011; Urban et al. 2010). This design was applied to develop the mathematical correlation between the molar ratio, pH and calcination temperature, which were selected as critical factors and named as X_1 , X_2 , X_3 respectively, with levels as given in Table 4.1. The response Y (particle size) was related to the three factors and can be described by the polynomial equation (3.1).

Table 4.1 Parameters and levels of D-optimal design

Independent variables	Factor levels			
	X_1	-1	0	+1
Molar ratio	X_1	1	2	3
PH	X_2	1	3	5
Calcination Temperature ($^{\circ}\text{C}$)	X_3	400	500	600

The total number of experimental runs was 18 for the D-optimal design as given in Table 4.2 (with error < 5%). The effects of the interaction between all the factors to produce the smaller sized ZnO NP were evaluated through an analysis of variance (ANOVA) of the final results from the D-optimal design. Moreover, it was important to check the adequacy of the model using diagnostic graphs and to validate the model by confirming the optimum experimental conditions as previously reported (Zhang et al. 2009).

In this study, the molar ratio of zinc acetate to oxalic acid (mol Z_{AC} : mol OX_{AC}) was varied between the range of 1 to 3, while the zinc acetate was maintained at 1 mole. The pH of the reactant solution was varied from 1.0 to 5.0 ± 0.2 using hydrochloric acid and ammonia solutions. All the experiments were based on the D-optimal design for the synthesis of ZnO NP and were carried out in a 500 ml three-

necked round bottom glass reactor under refluxing conditions at 65 ± 5 °C with ethanol as a solvent. The average size of the ZnO NP (crystal size) and the resulting structure were analysed using X-ray diffraction in the 2θ scan range of 20 – 80° , and the particle size of the ZnO NP was evaluated using a transmission electron microscope (TEM). Generally, the main steps for the optimization of the synthesis, which include fitting the model, checking the adequacy of the model, plotting the response surface and predicting the response (validation of the model), describe the influence of all factors on the size of the ZnO NP.

Table 4.2 Experimental runs of D-optimal design with Actual

Std	Run No.	(X ₁)	(X ₂)	(X ₃)	Size (± 2 nm) (A _{Actual})	Size (nm) (Y _{Predicted})
1	12	3	5	400	31	29.58
2	8	3	5	600	52	48.56
3	17	1	5	600	48	46.40
4	7	3	1	600	51	49.32
5	11	1	1	500	26	26.51
6	9	2	5	500	32	31.86
7	13	2	3	600	43	44.98
8	3	3	3	500	41	42.00
9	2	3	1	400	27	30.04
10	16	1	3	400	33	31.39
11	6	2	2	450	30	28.15
12	4	1	1	400	23	21.28
13	15	1	5	400	28	31.79
14	5	1	1	600	34	36.20
15	10	1	5	600	48	46.40
16	14	3	51	400	31	29.58
17	18	3	1	600	51	49.32
18	1	3	5	600	43	48.56

4.2.1 Model Fitting of D-optimal Designs

The effects of all the factors on the size of the synthesized ZnO NP were investigated using the quadratic polynomial model. The final model of optimization was estimated based on the experimental results of the D-optimal design with the respective coefficients as given in Equation (4.1):

$$\begin{aligned}
Y_{P,S} = & 49.67907 - 18.58686X_1 + 11.43100 X_2 - 0.15878X_3 + 4.99530X_1^2 - 1.21400 X_2^2 \\
& + 2.22835E-004X_3^2 - 1.37088X_{12} + 0.010896X_{13} - 3.73980E-004X_{23}
\end{aligned}
\tag{4.1}$$

The predicted model that was created by the D-optimal design involved all the coefficients which were shown as a quadratic regression. The size of the particles using the model at each point of the experiment are listed in Table 4.2 as a comparison between the theoretical (predicted) and the experimental results. The analysis of variance (ANOVA) results of the D-optimal model is given in Table 4.3. The degree of significance of the model and all the factors (X_1 , X_2 , and X_3) are presented according to the P -value, where a value that is less than 0.050 is considered to be significant, and any other value that is greater than 0.050 is not significant.

The significant factors are the molar ratio (X_1), the pH (X_2), and the calcination temperature (X_3) as well as the interaction between the molar ratio and the pH (X_{12}). Other important terms are the accuracy and variability of the model, which can be estimated according to the R-Squared (R^2) value which is between 0 to 1, with a value closer to 1 being a better prediction of the response (Kaushik et al., 2006). The R^2 of the D-optimal model showed a higher value, which was 0.9380. On the other hand, the Adj R-Squared (R^2_{adj}) coefficient was also found to be 0.8682, which was close to the R^2 value, and this value indicated a good correlation between the factors of the process using the D-optimal design. Adequate precision is a term that is used for evaluating the predicted range of responses relative to the associated error, where a value that is greater than 4 (10.633) is required to support the fitness of the model (Korbahti et al. 2009).

Table 4.3 ANOVA results for quadratic model of ZnO NP

Source	Sum of squares	Degree of freedom	Mean square	F-value	P-value
Model	1513.88	9	168.21	13.44	0.0006
X ₁	105.85	1	105.85	8.46	0.0196 *
X ₂	76.09	1	76.09	6.08	0.0390*
X ₃	920.03	1	920.03	73.51	< 0.0001*
X ₂₁	42.57	1	42.57	3.40	0.1024
X ₂₂	49.64	1	49.64	3.97	0.0816
X ₂₃	10.45	1	10.45	0.84	0.3875
X ₁₂	91.39	1	91.39	7.30	0.0270
X ₁₃	14.43	1	14.43	1.15	0.3142
X ₂₃	0.062	1	0.062	4.993E-003	0.9454
Residual	100.12	8	12.52		
Lack of fit	59.62	4	14.91	1.47	0.3585**
Pure error	4.50	4	10.13		
Total	1614.00	17			

*Significant at < 0.05% level; ** Not significant, $R^2 = 0.9380$, $R^2_{adj} = 0.8682$, Std. Dev. = 3.45, Mean=37.33, C.V= 9.48, Adeq Precision=10.633.

4.2.2 Adequacy Check of the Model

All the plots for investigating the optimization of ZnO NP synthesized using the D-optimal design are given in Figure 4.1. The studentized residuals with normal probability show that all points were close to the line, which indicates that there were no obvious problems with the normality of the design. The general effect of the plots between the studentized residuals and the predicted size was the random scattering of all the points rather than a funnel-shaped pattern, which confirms that the response had an original observation of variance and that there was no problem with the response variable (Rauf et al. 2008). The values of the studentized residuals were almost at intervals of between -3.5 to +3.5, and the observed response value was not considered for any value beyond these values (Korbahti et al. 2008). This model had a studentized residual value that was lower than ± 3.5 , which gives a good fitting of the model to the response surface. The outlier of the experimental runs clearly showed that all the points in the range of the outlier had a good distribution for the D-optimal design. The actual value of the size from the experimental runs was nearly the same as the value predicted by the model, which was evaluated by approximating the terms of R^2 and R^2_{adj} .

Table 4.3 shows that the correlation coefficients (R^2 and R^2_{adj}) did not exhibit high values which might have resulted from these insignificant terms. These results show that the three factors that had been selected with their levels to investigate the major effects on the synthesis of a smaller sized ZnO NP responded to the process.

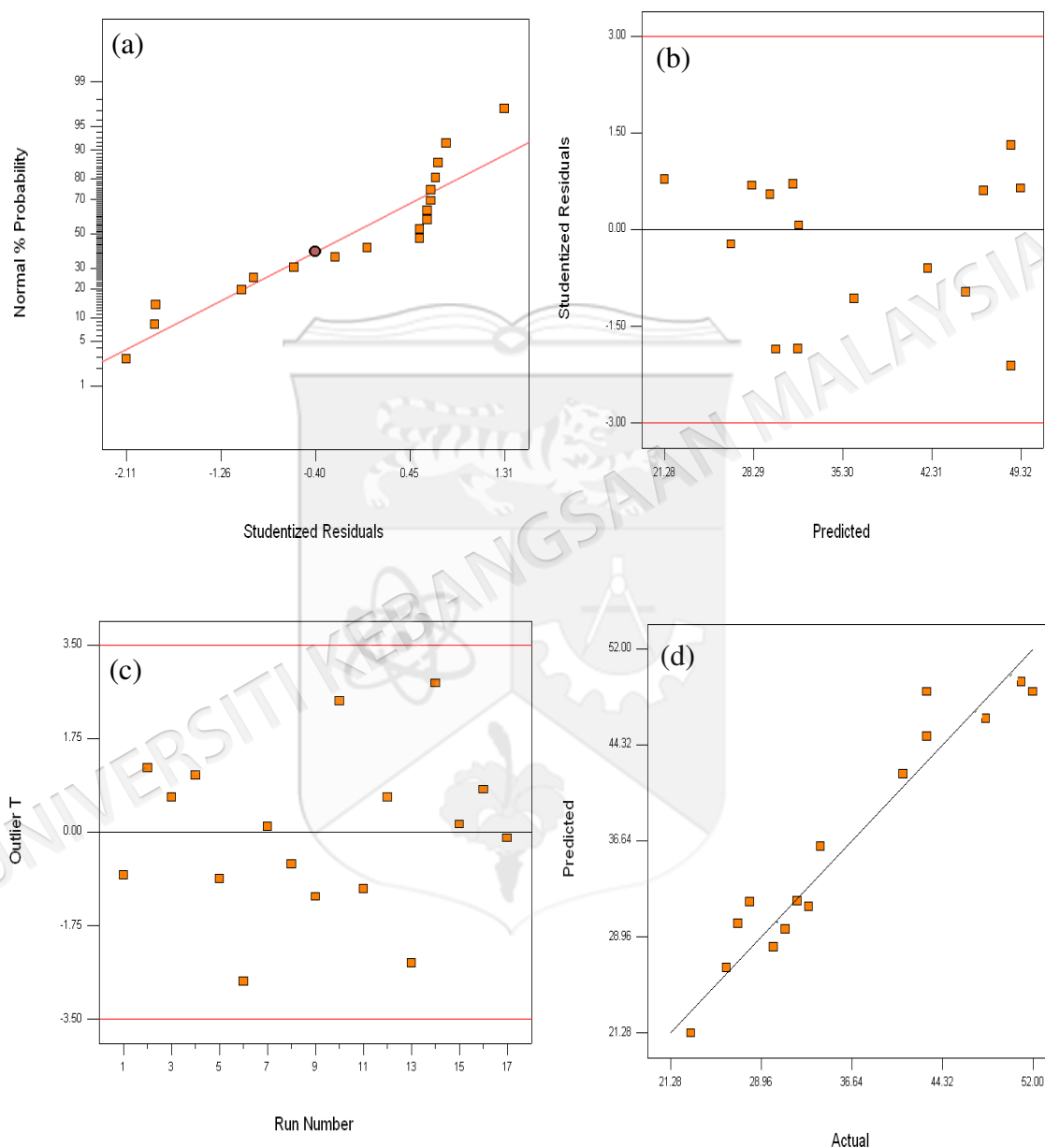


Figure 4.1 All diagnostic plots of optimization ZnO NP process using D-optimal design, (a) Normality, (b) Studentized residuals, (c) Outlier T, (d) Actual and predicted size of ZnO NP.

4.2.3 Response Surface Plotting s and Optimization

The effects of the molar ratio, the pH, and the calcination temperature on the size of the ZnO NP using the sol gel method was investigated by the RSM based on a D-optimal design. 3-D response surfaces and contour graphs were used to illustrate the effects of the interaction between each of the two factors of the starting materials, that is, the pH and the calcination temperature, on the size of the ZnO NPs as shown in Figure. 4.2.

It can be observed that the size of the ZnO NP increased as the pH increased from 1.0 to 3.0, and that subsequently above this value the size decreased slightly at a pH of 5.0 as shown in Figure 4.2 (a, a₁). The main reason for this behaviour was because the incompletely ionized oxalic acid and ammonia (for the pH adjustment), as the cross-links or bridges between the two Zn²⁺ ions, reacted to form a three-dimensional complex which inhibited faster particle growth (Yu et al. 2007).

Similarly, the effect of the molar ratio of Z_{AC}: OX_{AC} on the size of the ZnO NP was observed. The size was found to decrease as the molar ratio increased from 1:1 to 1:2, but gradually increased as the ratio increased to 1:3. This phenomenon is probably due to the complete reaction of oxalic acid in the mixture, in addition to the appropriate amount of acid, which prevented it from the forming an aggregation (Zhang et al. 2009). The minimum value of the particle size was obtained with a molar ratio of 1:2. The effects of the molar ratio and pH are exhibited clearly by 3D graphs, which attribute greater effects of pH and molar ratio when these are working together. These results indicated the significance of the interaction between the molar ratio and pH (X_{1,2}) from the model, which had a p-value of less than 0.05 (Kim et al. 2007). However, the effects of the calcination temperature and molar ratio on the size of the ZnO NP were investigated and the results are represented in Figure 4.2 (b, b₁). It appears that there was a linear relationship between the calcination temperature and the molar ratio as well as an increase in particle size as the calcination temperature was increased. The size of the particle increased rapidly as the temperature was increased from 400 to 600°C, indicating that significant effect when the temperature exceeded the optimum limit at 400°C.

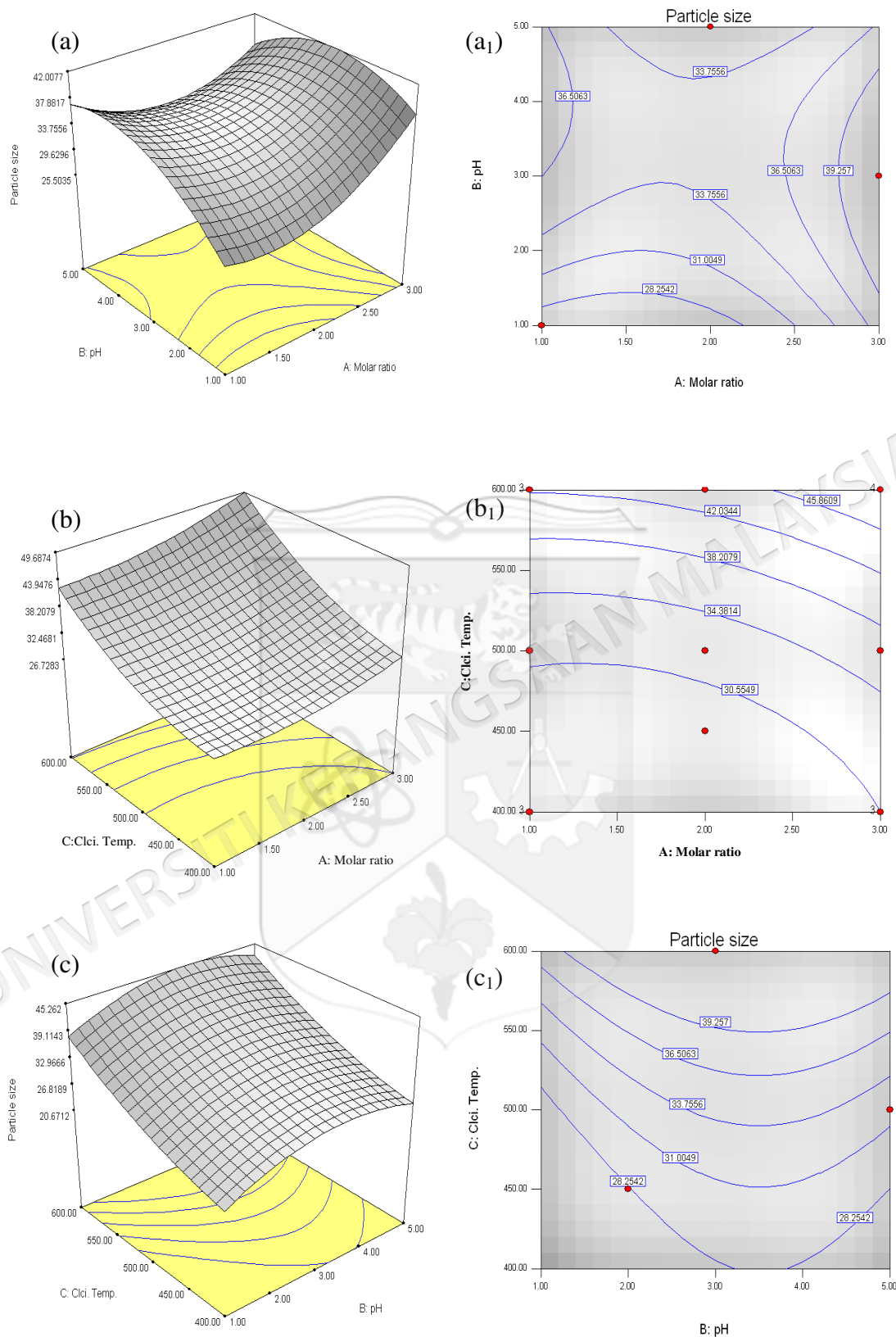


Figure 4.2 The effect of the molar ratio, pH and calcination temperature on the particle size of ZnO NP for the D-optimal design.

These results could also imply that the increase in size was mainly due to the aggregation of the particles to each other to become bigger, as reported in previous study (Chen et al. 2009).

Finally, the effects of the pH and the calcination temperature on the size of the ZnO NPs are shown in Figure 4.2 (c, c₁). It indicates that the pH and calcination temperature had a greater influence on the size of the ZnO NP when they were coupled together. The size of the ZnO NP varied sharply with an increase in the pH value from 1.0 to 5.0±0.2 and in the calcination temperature from 400 to 600°C. This phenomenon was observed earlier by several studies which reported that the pH and the calcination temperature were factors that strongly affected the size of ZnO NP using the sol gel method (Chen et al. 2009; Alias et al. 2009). The 3D graphs of the surface response of the relationship between the molar ratio and the pH with the calcination temperature showed that the D-optimal design was better for the optimization process. The effects of the molar ratio, pH, and calcination temperature were exhibited very clearly by the D-optimal results, which may be attributed to a good interaction between these factors to produce more accurate results of a smaller size in response (Myers & Montgomery 2002). On the other hand, the D-optimal design has been reported to be a common design that is used for the selection of an optimal set of experiments by analysing the data variance for different areas of application (Arroyo et al. 2011; Urban et al. 2010). A study of the effect of the factors on the response is considered as a statistical study which needs to be confirmed by more analytical data using different instruments. For further explanation and investigation of these results, the XRD, FESEM, TEM, UV-vis, and BET of the surface area were employed for each factor under different conditions. All the results of the experiments that investigated the effects of the factors by the D-optimal design have been summarized and will be discussed in the next chapter.

4.2.4 Model Validation and Experimental Confirmation

After the RSM based on the D-optimal design performance of the target response model, the optimum conditions for the creation of smaller sized ZnO NP were investigated for all the factors, as shown in Figure 4.2. The validation step indicates that it is very important to check the stability of the model for the selected factors of

the process. Generally, the desirability function is applied to investigate the validity of the predicted model in order to determine the optimal conditions for the production of smaller sized ZnO NP.

A numerical optimization of the Design of Experiments (DOE) software was selected to obtain the maximum value of the desirability function ($D = 1.000$) according to the location of the specific points of the controlling factor. The determination of the smaller sized ZnO NP consisted of five optimization criteria, namely, none, maximum, minimum, target and within range, which determined all the factors within the range with a minimum response as shown in Table 4.4.

Table 4.4 Optimization of all factors to obtain smaller particle size of ZnO NP

Parameter	Aim	Lower limit	Upper limit	Lower weight	Upper weight
Molar ratio	In the range	1	3	1	1
pH	In the range	1	5	1	1
Calcination Temperature (°C)	In the range	400	600	1	1
Particle size(nm)	minimize	23	52	1	1
D-optimal					

For the optimization of all the factors to produce a smaller size, the range and the minimum options were selected for all the factors and response, respectively. The predicted conditions for all the factors for a minimum size of ZnO (response) are illustrated in Figure 4.3.

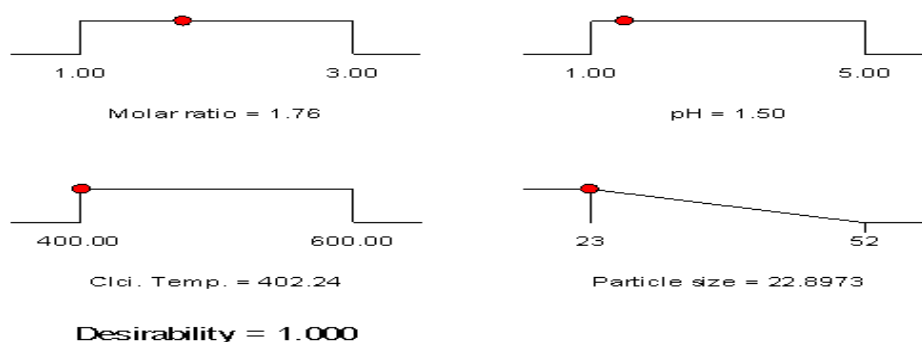


Figure 4.3 Predicted particle size, as obtained from the RSM based on D-optimal design under optimal conditions.

By applying the optimum conditions and by running the experiments, a smaller particle size of 18 nm was produced, which was close to the size of 22.89 nm predicted by the model. At the same time, the experiments were carried out at a molar ratio of 1:2, pH = 2.0 ± 0.2 (without adjustment) and calcination temperature of $400 \pm 2^\circ\text{C}$ with triple replications, and a final size of 18 ± 2 nm was obtained. According to the optimization results (comparison between the predicted and experimental results), more evidence pointed to the D-optimal design for the synthesis of smaller ZnO NP, and this was attributed to the good interaction between the selected runs of the experiment. Moreover, as has been reported, at an appropriate choice of range levels, all the factors were shown to play an important role in the optimization process (Rauf et al. 2008; Salimon et al. 2012). In this study, the range levels of the molar ratio, pH and calcination temperatures were evidently a good selection, as reflected in the close results obtained between the predicted and the experimental values.

4.2.5 Characterizations of ZnO NP

The X-ray diffraction pattern of the ZnO NP sample prepared through the sol gel method under the above-mentioned optimal conditions is shown in Figure 4.4 (a). It was observed that all the peaks of the ZnO NP were indexed as having a hexagonal wurtzite structure of ZnO (lattice parameters, $a = b = 0.3249$ nm, $c = 0.5206$ nm) and that the diffraction data agreed well with the Joint Committee on Powder Diffraction Standards (JCPDS) card for ZnO (JCPDS 36-1451) with all (20) the peaks at 31.86° (100), 34.54° (002), 36.32° (101), 47.62° (102), 56.66° (110), 62.96° (103), 68.04° (112), and 69.18° (201) being observed. The average particle size (crystal size) of the ZnO NP was estimated based on the Scherrer Equation (Cullity & Stock 2001) as given in Eq.3.2. The average particle size of the ZnO NP determined by XRD and TEM were found to be 18 and 20 ± 2 nm, respectively, using the optimum experimental conditions.

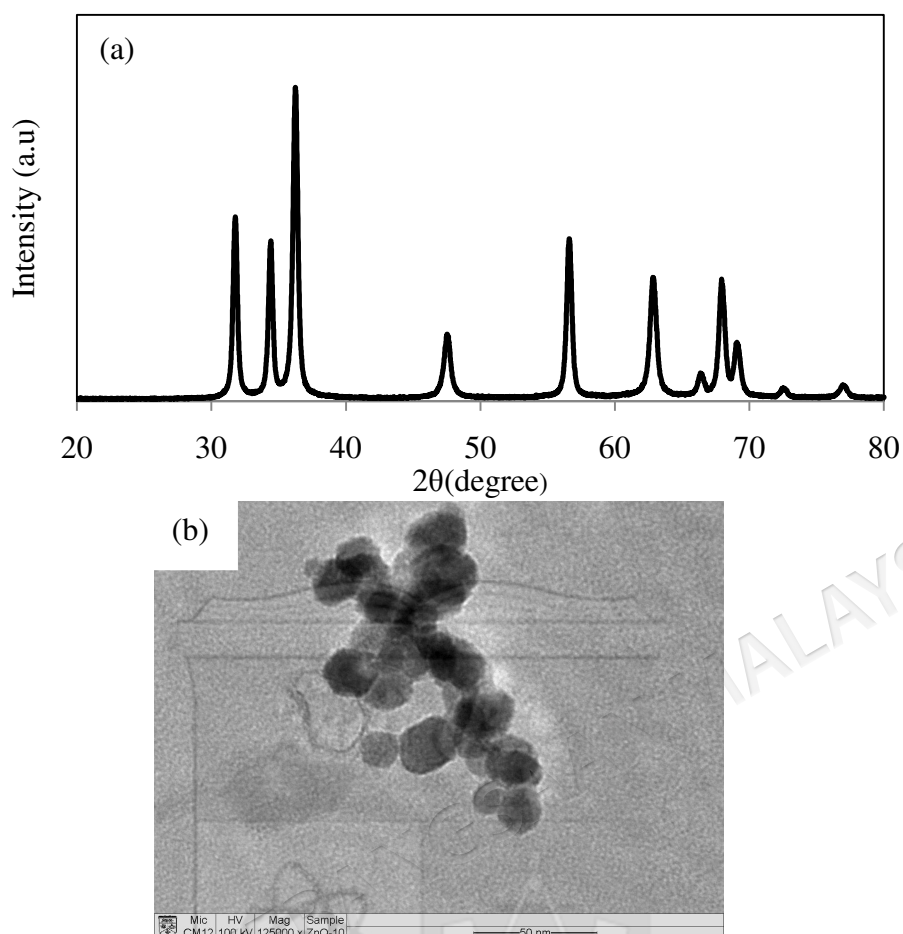


Figure 4.4 ZnO NP characterization (a) XRD pattern of ZnO NP (b) TEM image under optimal conditions of D-optimal design.

All the results in this study have indicated that the optimization of the process parameters for the synthesis of the ZnO NP has been achieved based on the use of the D-optimal design. The average particle sizes of ZnO NP using various preparation methods have been compiled and these results have been compared with the results of the present study as given in Table 4.5. The small sized ZnO NP was obtained through the sol gel method due to the flexibility of the method in producing nanoparticles with various properties compared to other synthesis methods (Sanchez et al. 2009). This study shows that smaller sized nanoparticles may be produced merely by controlling the parameters using the D-Optimal design without having to add a capping agent.

Table 4.5 Comparison of ZnO particle size prepared by different methods

Method	Capping agent	Using DOE	Shape of particle	Average Particle size	Ref.
Polyol	Yes	No	Spherical	19.6-68 nm	Chieng & Loo 2012
Precipitation	No	No	Spherical	42 nm	Goswami & Sharma, 2010
Precipitation	No	No	Spherical	47 nm	Hayat et al. 2011
Direct thermal	No	No	Spherical	32 nm	Labuayai et al. 2009
Mechanochemical	No	No	Spherical	50 nm	Stankovic' et al. 2011
Sol-gel	Yes	No	Spherical	>25 nm	Fernandes et al. 2009
Sol-gel	Yes	No	Spherical	27 nm	Zhang et al. 2009
Sol-gel	Yes	No	Spherical	35 nm	Uthirakumar & Hong 2009
Hydrothermal	Yes	Yes, Box Behnken	Spherical	55-110 nm	Ismail et al. 2005
Sol-gel	Yes	Yes, Taguchi (robust)	Spherical	30 nm	Kim, et al. 2007
Sol-gel	No	Yes, D-Optimal	Spherical	20 nm	This study

By using the same method (sol gel) but without utilizing the design of experiment, a bigger particle size was produced with the addition of a capping agent or surfactant as shown in Table 2.3. The bigger sized particle obtained by using the sol gel method can be attributed to the lack of optimum conditions of the parameters during the preparation process. In this study, the use of the D-Optimal design and the verified experimental runs led to the minimization of the particle size via the optimization of the process parameters through the sol gel preparation method. The D-Optimal design has never been used for the synthesis of ZnO NP before, but now its ability to widen the absorption band gap due to the smaller particle size makes it possible for it to be used in the photocatalytic degradation of some recalcitrant organic pollutants that are found in industrial wastewater (Sakkas et al. 2010; Bahadir et al. 2008; Bahadir et al. 2009). It can be concluded that the best desired results for the response (target) would be produced by combining the experiments for the catalyst

preparation with one of the simulation designs. Therefore, through this procedure, the control and understanding of any changes to the process can easily be made through the DOE method, which could assist in scaling up the design of the nanoparticle production to be more economically feasible.

4.2.6 Validation of Optimum Condition for Other Metal Oxide

After the validation of the synthesized model of the ZnO NP created by the DOE based on the D-Optimal design, about 5 metal oxides were produced using the optimum conditions of molar ratio, pH, and calcination temperature. The starting materials, final oxide, and calculated particle size by XRD and TEM are summarized in Table 4.6.

Table 4.6 Particle size of several metal oxide synthesized by sol gel using optimum conditions of D-optimal design.

No	Starting material	Formula of final metal oxide	Particle size by XRD (nm)	Particle size by TEM (nm)
1-	Copper (II) acetate	CuO	17	18±2
2-	Iron (III) acetate	α -Fe ₂ O ₃	23	24±2
3-	Cobalt (II) acetate	Co ₃ O ₄	21	23±2
4-	Titanium (IV) isopropoxide	TiO ₂	22	24±2
5-	Nickel (II) nitrate	NiO	24	26±2

All the particle sizes of the metal oxides produced were very close with the predicted size obtained from the D-Optimal design. The predicted value of the size from the D-Optimal design was about 22.89 nm compared to 22±4 nm for all the metal oxides. One advantage that was observed of the optimization process was that all the metal oxides produced had a spherical shape, as shown by TEM in Figure 4.5 (with magnification of 100 to 125 K). The spherical shape of these oxides indicates that a higher surface area can be produced (Pathak & Purohit 2013). At the same time, a higher surface area enhances the oxide activity for applications by increasing the reaction rate at the surface (Shinde et al. 2011; Shukla et al. 2010).

The crystallinity of all the metal oxides, as given in Figure 4.6, was evaluated using the XRD. The XRD patterns of all the oxides were matched against the patterns of the Joint Committee on Powder Diffraction Standards (JCPDS) with no impurities using EVA software (version 2) and the XRD pattern of each oxide was labelled. These results indicate that the optimization of the sol gel parameters using the DOE is a good way to produce different metal oxides of high quality and quantity at a lower cost. Furthermore, overall the investigations help to scale up the process in future for many applications with safer environmental impacts.

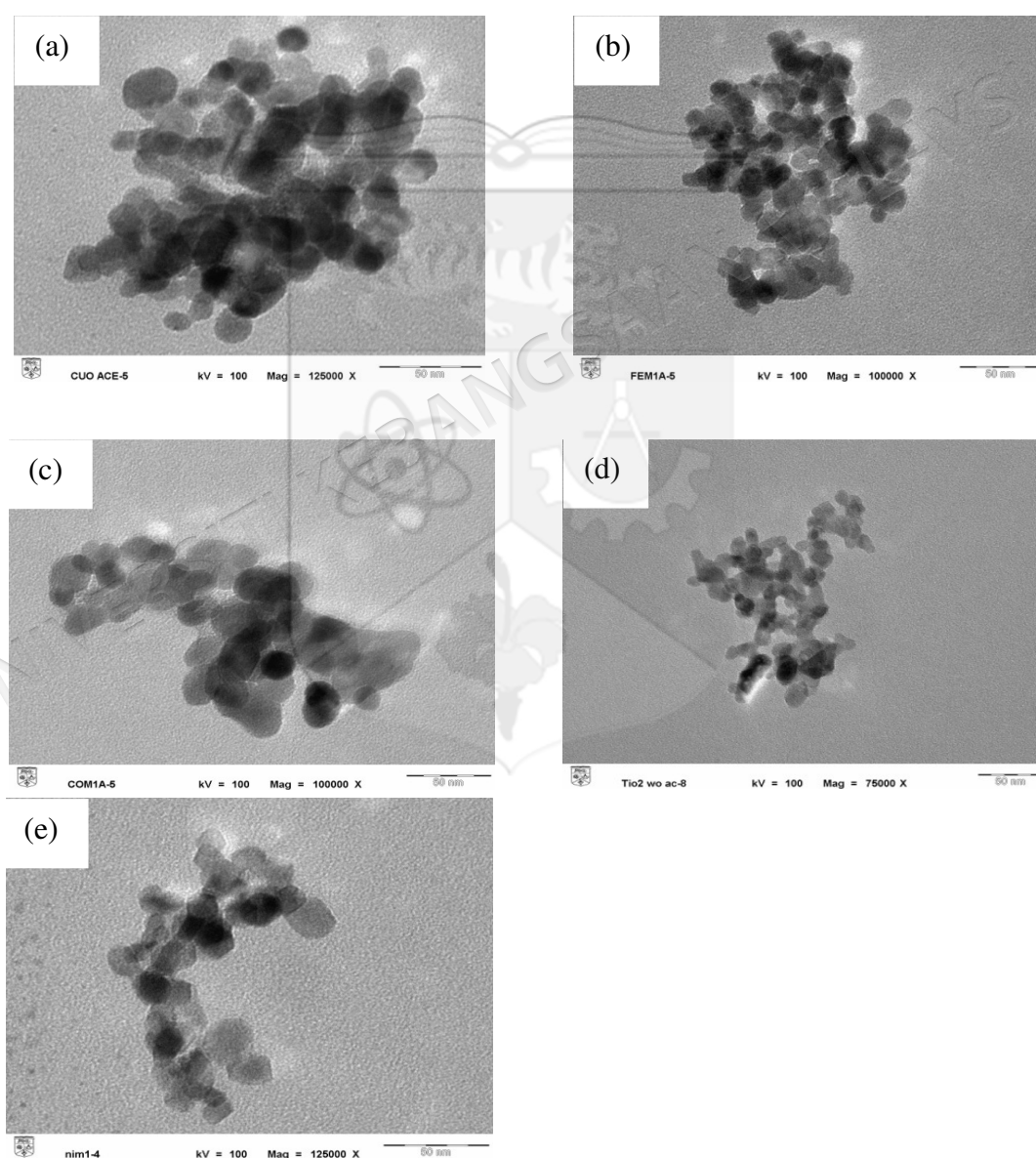


Figure 4.5 TEM images for different metal oxide prepared by sol gel under optimum conditions, (a) CuO, (b) α -Fe₂O₃, (c) Co₃O₄, (d) TiO₂, (e) NiO.

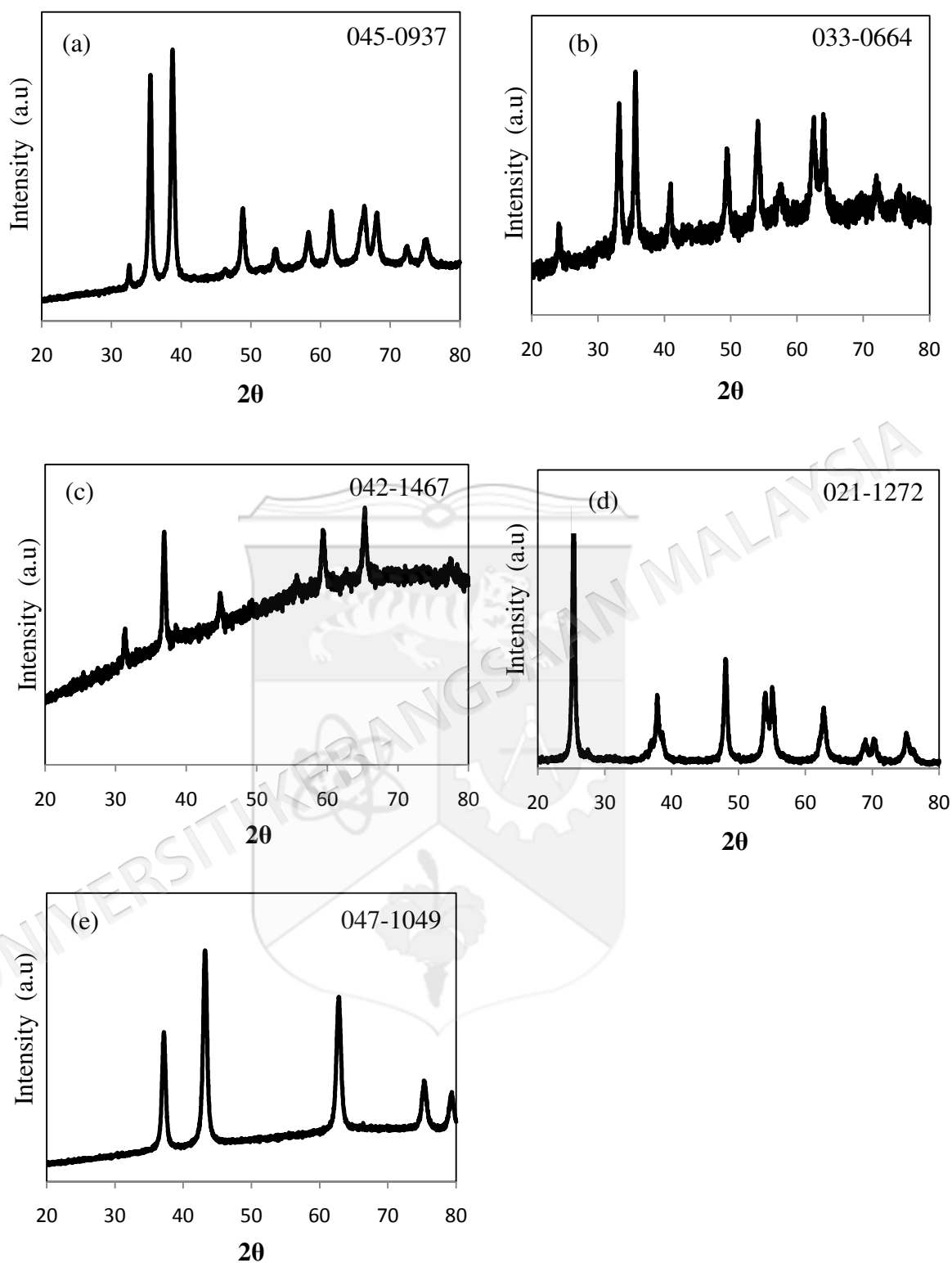


Figure 4.6 XRD patterns of different metal oxide with JCPDS standard prepared by sol gel under optimum conditions, (a) CuO, (b) α -Fe₂O₃, (c) Co₃O₄, (d) TiO₂, (e) NiO.

After the optimization process using RSM based on D-Optimal design, the analysis and characterization under conditions of synthesized ZnO NP using several instruments in order to investigate the properties of ZnO NP. These characterizations provide detail explanation about the effect of selected factors (molar ratio, pH and calcination temperature) on the size and properties of ZnO NP which is supported the statistical method to finalize the synthesized process of ZnO NP optimum conditions. To test thermal stability (final decomposition) of precursor of ZnO and doped ZnO NP under different of conditions, a thermogravimetry-differential scanning calorimetry (TGA-DSC) was used. To estimate crystal size of ZnO and doped ZnO NP an X-ray diffractometer (XRD) was applied. The surface morphology of these oxides was viewed using the field emission scanning electron microscope (FESEM) and transmission electron microscope (TEM). Moreover, the absorbance of all samples to determine the band gap was evaluated by UV/Vis spectrophotometer at room temperature. All of these analyses can provide idea about the condition to perform an efficient photocatalyst for detoxification under direct solar radiation.

4.3 THERMAL ANALYSIS

4.3.1 Undoped ZnO NP Precursors

The TGA-DSC spectrum for a typical zinc oxalate precursor powder of shown in Figure 4.7. DSC spectra of the samples synthesized with the molar ratio 1:1 and 1:2 (maintained at pH of 2.0 ± 0.2) consisted of two endothermic peaks as observed in the heating profiles of Figure 4.7 (a) and (b). The first endothermic peak observed below 190°C corresponds to the evaporation of ethanol and the remaining water while the second peak could be attributed to the thermal decomposition of zinc oxalate according to the equations (4.2 – 4.6) below (Yang et al. 2005). Two weight losses in the temperature range between 60 and 420°C were also observed with the first weight loss experienced by the sample prepared with a molar ratio of 1:1 and 1:2 occurring between 120°C and 190°C , which correspond to 19.0% and 17.9% lost, respectively. This percentage lost in agreement with the theoretical calculated to be 19.05% by the zinc oxalate dehydration. The second weight loss corresponding to a further 42.0% and 36.1% lost, respectively, was observed between temperature of 360 – 420°C , which could be attributed to the decomposition of zinc oxalate to ZnO (Lin et al. 2003; Yang

et al. 2005). The extra weight loss occurring in the sample prepared at a 1:1 ratio was observed due to the excess of unreacted zinc acetate, indicating that the amount of oxalic acid added at a 1:1 ratio was inadequate for completion of the zinc acetate-oxalic acid reaction. The zinc acetate decomposition (Appendix F, TGA analysis), which is supposed to be at 360°C but it was shifted to around 400 °C, due to the presence of entangled networks formed in the zinc oxalate (Sarawuth et al. 2009). For this reason the zinc acetate decomposition occurred at the same decomposition temperature as that of the zinc oxalate.

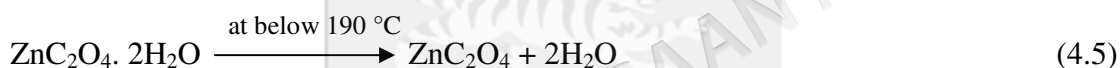
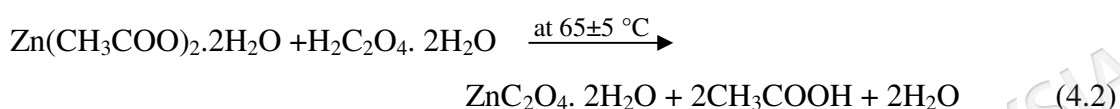


Figure 4.7 (c) shows that four endothermic peaks were observed via DSC analysis of the sample prepared at a molar ratio of 1:3. The first peak observed could be attributed to the release of ethanol from zinc oxalate and oxalic acid molecules, while the second peak is due to the removal of water molecules. The third peak attributed to the decomposition of excess unreacted oxalic acid (Appendix F, TGA analysis) ranging between 200 to 360°C constituting the zinc oxalate molecules. The last peak observed at 420°C with slight shift corresponds to the decomposition of zinc oxalate due to mixing with the unreacted oxalic acid. Different weight loss percentage was observed over the same range of temperatures with approximately 3% of weight loss was determined to occur below 65°C corresponding to ethanol evaporation, while 15% lost over the temperature of 120 to 190°C which indicates the complete removal of water. Finally, approximately 37.1% of the sample weight was lost in the last two peaks which indicate an increase compared to the sample prepared at a molar ratio 1:2 (36.1%) due to the presence of excess unreacted oxalic acid.

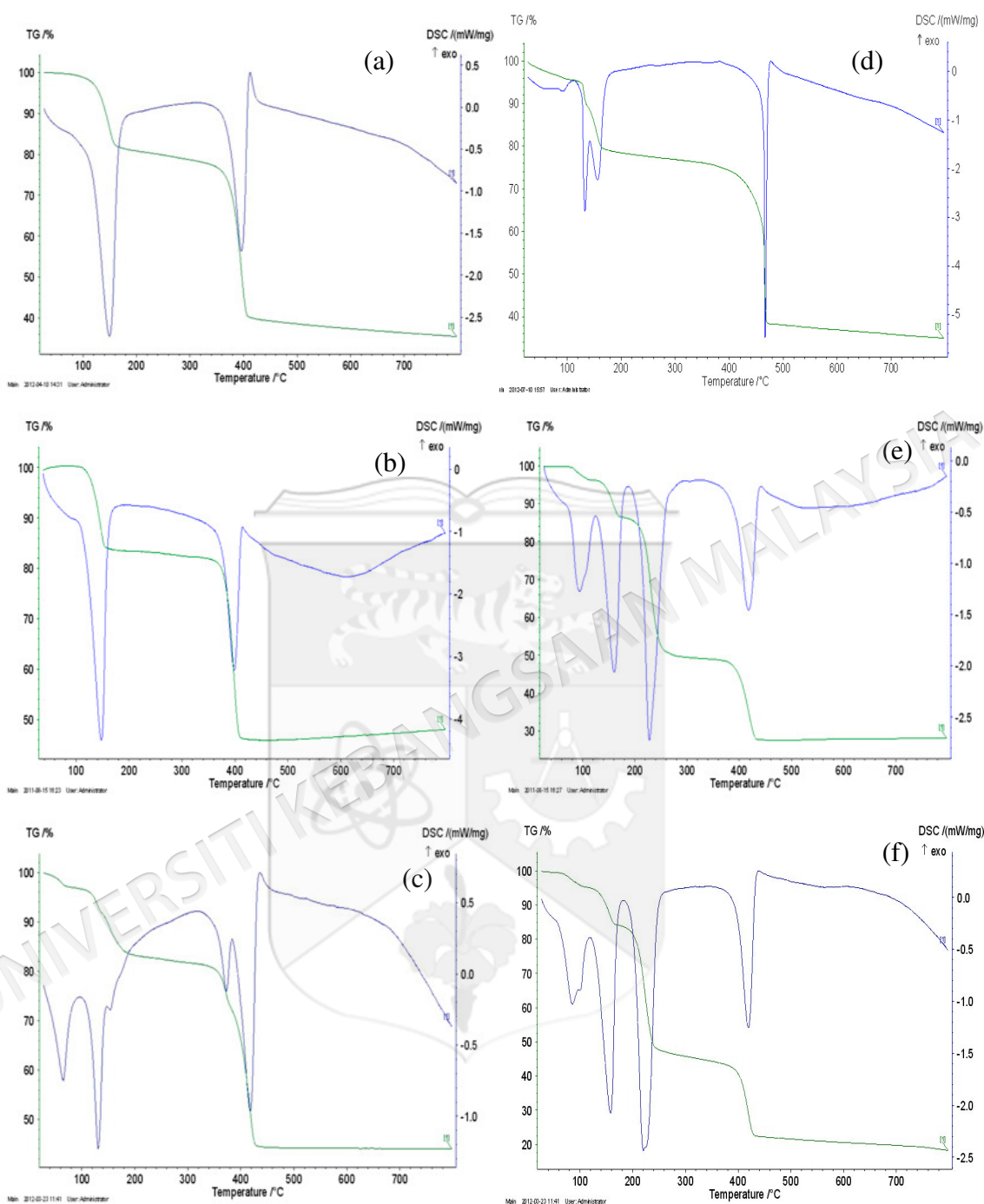


Figure 4.7 TGA-DSC spectra for thermal decomposition of zinc oxalate dehydrate, (a) ratio = 1:1 at pH of 2.0, (b) ratio = 1:2 at pH of 2.0, (c) ratio = 1:3 at pH of 2.0, (d) ratio = 1:2 at pH of 1.0, (e) ratio = 1:2 at pH of 3.0, (f) ratio = 1:2 at pH of 5.0.

The effects of pH when using ammonia were also investigated. The DSC analysis showed four endothermic peaks over a temperature range of 80 and 420°C as shown in Figure 4.7 (e) and (f). The first peak was observed at 80°C which is attributed to the release of residual ethanol mixed with a small amount of ammonia (Huang et al. 2005). Ammonia was decomposed into a mixture of nitrogen oxide gas and water at the second peak between 120 to 190°C. The third peak shows the presence of unreacted oxalic acid, which did not react with the zinc acetate in the presence of ammonia. Finally, the last peak at 420°C is indicative of the zinc oxalate decomposition. There was an increase in weight loss observed when the pH was adjusted from 3.0 to 5.0±0.2. The first weight loss of approximately 4% indicates a removal of ethanol-ammonia mixture while the second weight loss of approximately 10% corresponds to the release of water and ammonia mixture due to the different solubility of ammonia in ethanol and water solutions (Huang, et al. 2011). The presence of unreacted oxalic acid contributed to the third weight attributed to the ammonia forming complex chains between zinc acetate and oxalic acid that could have prevented further reactions from occurring between them. The decomposition of pure oxalic acid which is supposed to be observed at 200°C (Appendix F, TGA analysis) had deviated in the decomposition temperature to 220°C when ammonia was added. The weight losses of approximately 36% and 38% at temperature of 220°C, which is the final zinc oxalate decomposition temperature between 360°C to 420°C was found at weight loss of approximately 20% and 24% for pH of 3.0 to 5.0±0.2, respectively. The TGA run shows that the final ZnO product was stable up to a temperature 800°C. No weight loss was observed at temperature beyond 420°C indicating that the product, which is a crystallized ZnO nanoparticle as confirmed via XRD analysis.

4.3.2 Doped ZnO precursors

Thermal stability of doped ZnO NP with different Fe^{3+} , Sm^{3+} and Ti^{4+} ions using optimum of pure ZnO were investigated. Thermal behavior of the doped samples was studied using thermogravimetry-differential scanning calorimetry (TGA-DSC) analysis. Figure 4.8 shows the TGA- DSC curves for both ZnO and doped ZnO precursors prepared by the same method of sol gel and conditions. As can be

observed from the DSC curves of all samples a two endothermic peaks for the undoped ZnO, three peaks for doped particles by Fe^{3+} , Sm^{3+} and four by Ti^{4+} ions were observed in the heating profile with a corresponding loss of weight observed on the TGA curves. The first peak is smallest at 50 to 75 °C is attributed to ethanol lost and increasing with different of doping ions which attributed to the nature of the material used. Water removal was observed between the 100-140°C as the second peak. Another small peak below 190°C for the doped by Fe^{3+} and Sm^{3+} attributed to the releasing of nitrate (precursor of dopant) as nitrogen oxide (NO_x) and carbon oxide(CO_x) for Ti^{4+} when using the tetra-isopropoxide ($\text{C}_{12}\text{H}_{28}\text{O}_4$). Generally, the last peak could be attributed to the thermal decomposition of oxalate of all doping ions to ZnO NP.

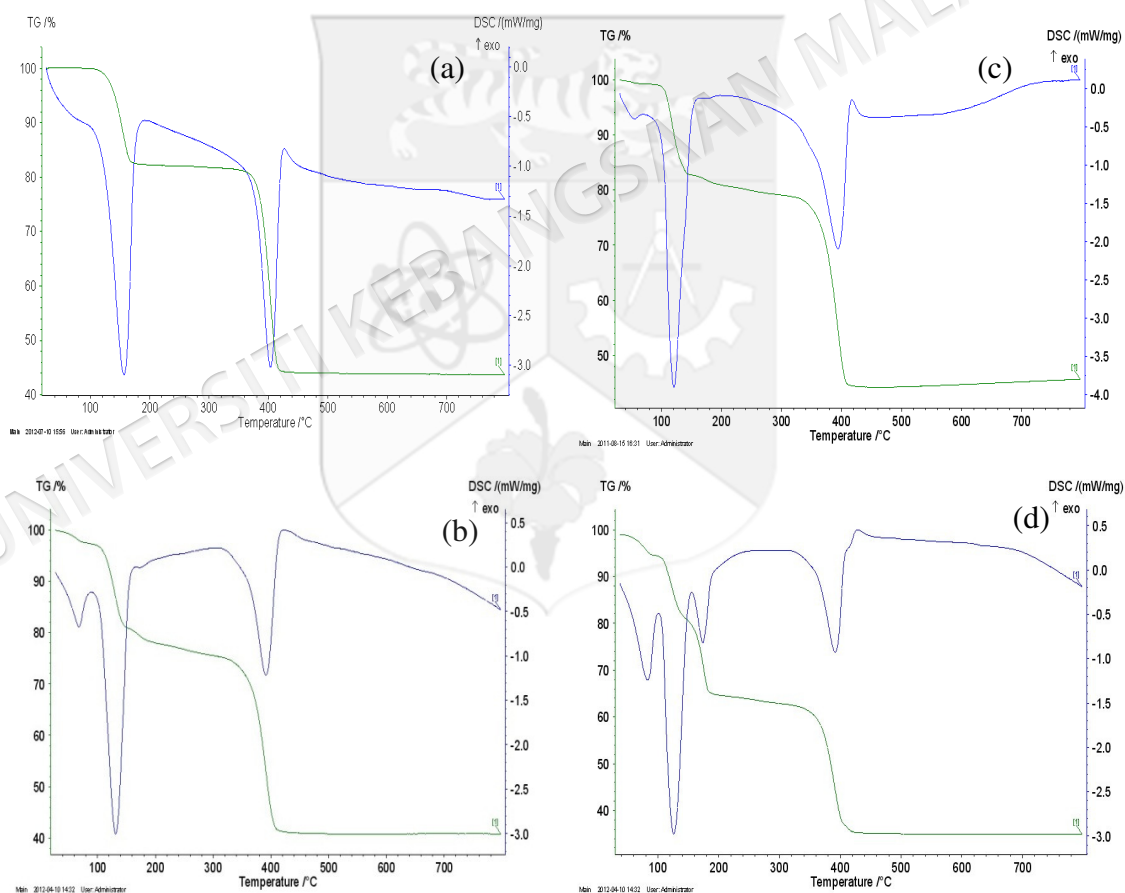


Figure 4.8 TGA-DSC curves of (a) undoped ZnO (b) 0.5 wt % Fe^{3+} doped ZnO (c) 0.5 wt % Sm^{3+} doped ZnO (d) 0.5 wt % Ti^{4+} doped ZnO NP sample.

The TGA curves of doped samples showed that there were four different weight loss for the complete thermal decomposition. All of the weight loss of ZnO and doped ZnO NP were calculated and listed in Table 4.7. The range of temperature was divided into four according the DSC curve which is the first for ethanol lost and these value increasing and may due to properties of cations (Fe^{3+} , Sm^{3+} and Ti^{4+}) for chelate or bond with a carboxyl groups (COOH) within the reaction of the oxalic acid with zinc acetate. The weight lost of second range between 100-140°C which was due to dehydration of water from oxalate (anhydrous zinc oxalate) according to Equation (5.3). The third weight loss at 140-200°C which closed results by using the iron and samarium nitrates as precursors of doping source of Fe^{3+} , Sm^{3+} and no any lost for undoped ZnO. However, when using the titanium tetra-isopropoxide ($\text{C}_{12}\text{H}_{28}\text{O}_4$), about 10 % weight lost was observed which may attributed to decomposition of tetra-isopropoxide with small amount of oxalic acid not reacted (Naeem et al. 2010).

Table.4.7 Weight loss of ZnO and doped ZnO NP precursors temperatures profile

Material/Temp. range	50 -75°C	100-140°C	140-200°C	200-420°C
ZnO	-	17.9%	-	36.10%
0.5 wt.% Fe^{3+}	1%	17%	1.9%	36.60%
0.5 wt.% Sm^{3+}	2.1%	18%	2%	36.57%
0.25 wt.% Ti^{4+}	4%	17%	10%	34%

The last weight loss of ZnO and doped ZnO NP occurs between 200-420°C which due to decomposition of zinc oxalates dihydrates before and after doping. The largest weight loss was obtained by decomposing of zinc oxalate anhydrous to ZnO before and after doping as shown in Figure 4.8 and summarized in Table 4.7 (Yang et al. 2005). These results of ZnO and ZnO doped with Fe^{3+} , Sm^{3+} were in good agreement with theoretical as reported recently (Ni et al. 2011). The difference in weight loss between the ZnO and doped ZnO NP due to the thermal decomposition of the additive of doping ions of iron and samarium nitrates and is closed to ≈ 0.5 wt. % compared to undoped ZnO NP. On the other hand, to confirm the presence of Fe^{3+} , Sm^{3+} in structure of ZnO and wt. %, XRD and EDX were used (Hu et al. 2005) and detailed explanation will be in next sections. The ions with nitrates source have been

reported in literature as best for doping process which may be due to easily insert to the ZnO lattice and decomposition at lower temperature (lower than 200°C). No further weight loss was observed by TGA at temperatures higher than 410 °C. This temperature is the point at which the thermal analysis of ZnO and doped ZnO oxalate dihydrates has completed, as reported by an earlier study (Lin et al. 2003).

4.4 X-RAY DIFFRACTION (XRD) ANALYSIS

To identify the structure and crystallite size of ZnO NP, the X-ray diffractometer was applied and compared with standard of Joint Committee for Powder Diffraction (JCPDS). The effect of the process parameters such as molar ratio, pH and calcination temperatures on the size of the ZnO NP was evaluated based on changing of crystal size. However, the doping of ions into the lattice structure of the ZnO NP was also investigated using X-ray diffractometer.

4.4.1 X-ray Diffraction of ZnO NP

Figure 4.9 shows the typical X-ray diffraction patterns of all reactants was used to synthesize of ZnO NP powder by sol-gel process under different experimental conditions such as pH solution and calcination temperature. The diffraction peaks of zinc acetate and oxalic acid before the reaction were matched with JCPDS Card No.033-1464 and 014-0832 respectively. After gel formation and drying at 80°C, the peaks of zinc acetate and oxalic acid were not detected, this indicates that the reactants were converted into zinc oxalate as observed. The diffraction peaks for zinc oxalate corresponding to the JCPDS Card No. 025-1029. At same time, the effects of temperature on structure was clearly observed, since all peaks of zinc oxalate was disappeared and convert to oxide (ZnO) as presented in Figure 4.9.

The diffraction peaks indicates the wurtzite structure and the hexagonal phase with $P6_3mc$ space group of ZnO NP after calcination at 400°C with lattice constants of $a = b = 0.32490$ nm and $c = 0.52060$ nm. The 2θ characteristic peaks of ZnO NP at 31.68, 34.36, and 36.18 and 56.56° corresponding to the (100), (002), (101) and (110) plane, respectively, of the crystal lattice. These values agree well with those provided by the standard card JCPDS 36-1451.

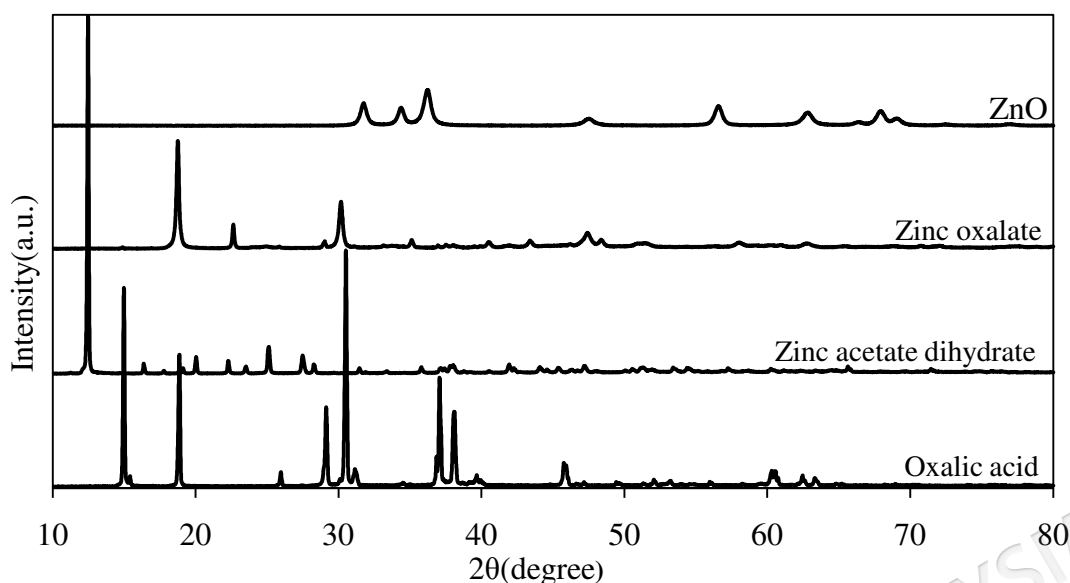


Figure 4.9 XRD analysis of the starting materials and ZnO NP after calcinations

The effect of molar ratio on size of ZnO NP was investigated and shown in Figure 4.10 (a). All peaks appear belong to ZnO NP with wurtzite structure and hexagonal phase and no peak for other phase or impurity. Clearly effects of molar ratio on crystallinity of ZnO which higher of 1:3 and lower of 1:1 molar ratio become sharper than middle of 1:2. According this observation the crystal size of 30, 18 and 35 ± 2 nm was found for 1:1, 1:2 and 1:3 respectively, by calculation using the Scherrer Equation (3.2). These results may attribute to the amount of oxalic acid which at low ratio of 1:1 IS shows not enough and at higher shows more than enough according the TGA-DSC results (Figure 4.7 (a,c)). The extra amount of zinc acetate (1:1) and oxalic acid (1:3) was influenced on the nucleation and growth of ZnO NP and controlled of size as reported in a pervious study (Hu et al. 2005).

In case of molar ratio of 1:2 with pH of 2.0 ± 0.2 indicates as the optimal ratio of zinc acetate to oxalic acid with complete reaction and confirmed by the weight loss by TGA-DSC (Figure 4.7 (b)), which in good agreement with the theoretical value (Yang et al. 2005). Additionally, the effect of molar ratio on size and shape of ZnO NP prepared by sol gel process using zinc acetate and sodium hydroxide have been reported (Nejati et al. 2011).

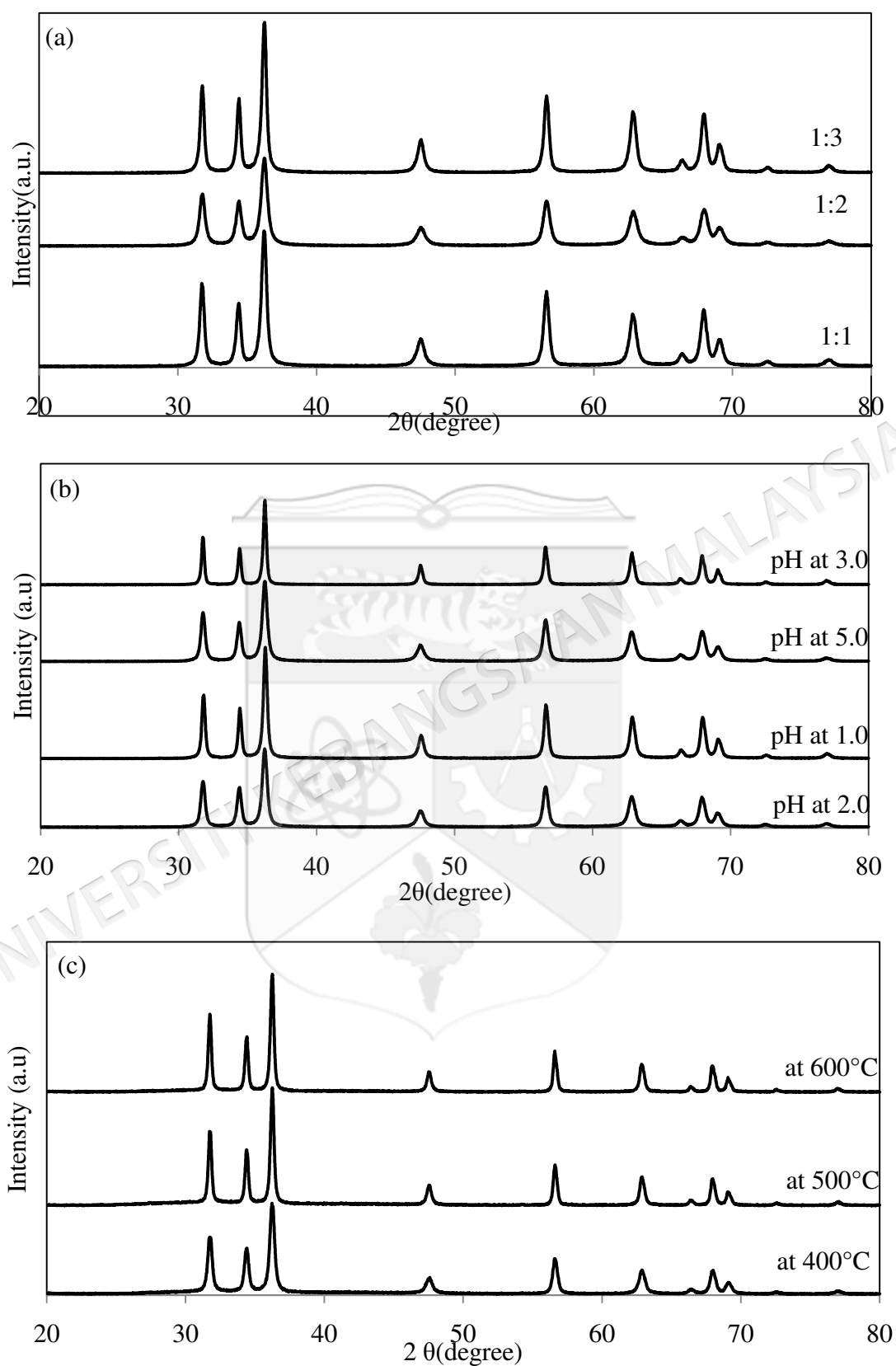


Figure 4.10 XRD analysis of (a) ZnO NP prepared in different molar ratio, (b) ZnO NP prepared at different pH, (c) ZnO NP at different calcination temperatures.

On the other hand, the effect of pH on the size of ZnO NP was investigated by adjusting the reactant solution with ammonia and hydrochloric acid. The crystal size of the ZnO NP was evaluated as shown in Figure 4.10 (b). All XRD peaks of ZnO NP synthesized at various pH values indicated that there was no change in the hexagonal wurtzite structure of ZnO NP. However, the crystallinity of the ZnO NP increases when the solution pH was adjusted at 1.0 and 3.0, whereas decreases when the pH was further adjusted to 2.0 and 5.0. At low pH of 1.0, which is below the optimal pH of 2.0 ± 0.2 (without adjustment), large particle sizes were observed of 34 nm. This results may be attributed to the presence of HCl (increase of H^+ ions) which inhibits hydrolysis and condensation reaction and leading to large particle (Figure 5.3(c)). Generally, within the adjusting pH for acidic or basic route, higher or lower than optimal, the limitation of ZnO nuclei in initial stage leading to increase of particle size. Similarly, the acidic route has been reported as appreciate solution under optimum value of pH for synthesis a smaller particle of ZnO NP (Zhang et al. 2009). A smaller particle of 18 ± 2 nm was obtained to achieve when pH value is 2.0 ± 0.2 , while at pH 3.0 ± 0.2 a bigger size of ZnO NP was obtained with size of 32 ± 2 nm. It is observed that as pH increases the particle size getting bigger. It was observed that upon the increase of the saturation of solution $Zn^{2+}/NH_3.H_2O$, the growth of particle became slower as reported in the earlier study (Zhang, et al. 2009). When the pH increases to 5.0 ± 0.2 , the particle size decreases because additional amount of ammonia resulted in the formation of stable Zn^{2+} complex with ammonia which helps to grow ZnO particle faster (Yu et al. 2007). The pH at 2.0 ± 0.2 without any additive for adjustment was the best for growth of ZnO NP faster (small particle) without any hampered by the additive of materials.

The effects of calcination temperatures on the size of ZnO NP at an optimal molar ratio of 1:2 and pH of 2 ± 0.2 are shown in Figure 4.10 (c). The optimal sample was calcined at different temperature of 400, 500 and 600°C. All the peaks of the ZnO NP are sharpened at a temperature greater than 400°C and no peak for impurity was appeared (Uthirakumar & Hong, 2009). These results shows the significant influence of temperature which was size increased from 18 to 35 ± 2 nm (by XRD) and from 20 to 40 ± 2 nm (by TEM). Increasing the size with calcination temperatures it may attributed to improve the growth of crystallite which it depended on XRD sharpness

(Kumar & Sahare, 2012). More description and discussion about the effects of molar ratio, pH and calcinations temperature will be reports in next sections.

4.4.2 X-ray Diffraction of Doped ZnO NP

After optimized all experimental condition to produce the smaller size of ZnO NP, doping with different ions namely Fe^{3+} , Sm^{3+} and Ti^{4+} in order to improve the properties ZnO NP. One of the improvements of ZnO NP by doping was decreased in crystal size and enhancement in the absorption in the photocatalyst application. Increase of surface area and shifting of XRD peaks position follows the decreasing of ZnO NP size which have been reported earlier (Paola et al. 2011).

Figure 4.11 (a) shows the XRD patterns of the ZnO and Fe^{3+} -doped NP with different of concentrations of Fe^{3+} as 0.0, 0.25, 0.5, 0.75 and 1.0 wt. % which were calcined at 400°C . The indexed diffraction peaks indicates a hexagonal wurtzite structure with space group ($P63mc$) for all samples and diffraction data also showed good agreement with the JCPDS card for ZnO (JCPDS 36-1451). Diffraction spectrums of the Fe^{3+} doped ZnO samples did not shows the presence of any peak for any compound of iron oxide such as α or γ - Fe_2O_3 or Fe_2O_4 . This could probably be attributed to the good dispersion of Fe^{3+} into the structure lattice of the ZnO NP or to the minute amount of Fe^{3+} dopant that was used (Liu et al. 2009).

On the other hand, the XRD peaks of Fe^{3+} doped ZnO were broad in comparison with the undoped ZnO NP, indicating that the Fe^{3+} doping into the lattice of ZnO which inhibited the crystallization of peaks (Liu et al., 2009). These results show that smaller particles grow more easily when incorporated with ZnO as reported earlier in other studies (Chen et al. 2008). This phenomenon can be attributed to the difference in size of the ionic radii of Fe^{3+} (0.064 nm) and Zn^{2+} (0.074 nm) ions (Srivastava et al. 2009). The lattice parameters of Fe^{3+} doped ZnO (0.5 wt. %) and ZnO NP were calculated from the XRD as $a = b = 0.32488$ nm, $c = 0.52056$ nm and $a = b = 0.32490$ nm, $c = 0.52060$ nm, respectively. Lattice parameters of Fe^{3+} doped ZnO were slightly less than those of ZnO, which confirming that the Fe^{3+} ions doped into the ZnO NP crystal lattice without changing the wurtzite structure phase. On the

other hand, the increasing of the lattice parameters of doped ZnO sample when using Fe^{2+} has been reported by Luo et al. (2010). The effects of Fe^{2+} ionic radii (0.77 Å) showed significant enlarge of the interatomic spacing to increasing the lattice parameters. The average crystallite size of the Fe^{3+} doped and ZnO NP was calculated using the Debye-Scherer equation and the data are presented in Table 4.8.

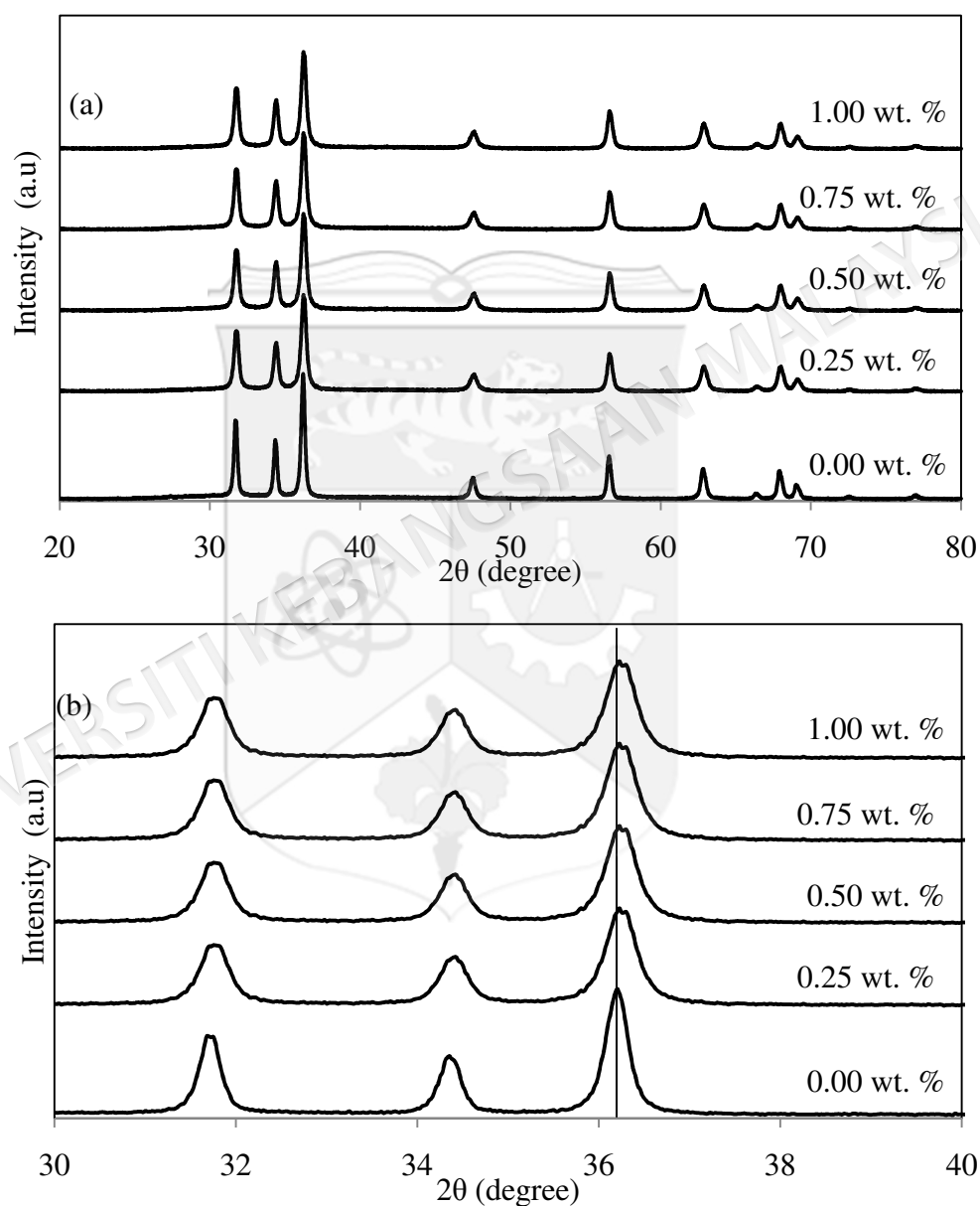


Figure 4.11 XRD patterns spectrum of (a) Fe^{3+} -doped ZnO NP with different concentration calcined at 400°C (b) shifted of peak (101) position is observable towards to right.

At same time, to confirm that doping of Fe^{3+} into lattice of ZnO by replacing Zn^{2+} in the matrix was obvious position of XRD pattern peak of (002) shifting as reported (Ahmed et al. 2012). The positions of peaks shift towards to right (high value of 2θ) with increasing of Fe^{3+} were observed as shown in Figure 4.11 (b). This result of shifted position peaks was reflected that doping of Fe^{3+} substitution Zn^{2+} in the cell of ZnO and change in the average of crystal size. The Fe^{3+} ions shows suitable for doped ZnO because easy to replace the Zn^{2+} cation vacancies as reported earlier (Karmakar et al. 2007). The shifting of peaks position to left (lower value of 2θ) when ZnO doped with Fe^{2+} has been reported to be attributed to the ionic radii of Fe^{2+} (0.077 nm) large than Zn^{2+} (0.074 nm) which caused to increases of lattice parameters (Panigrahy et al. 2012).

For Sm^{3+} -doped ZnO, the diffraction peaks for zinc oxalate was observed and no peak for samarium appear which most likely due to the low concentration of Sm^{3+} concentrations that were used. After calcination at 400°C , all the XRD peaks for the ZnO and Sm^{3+} -doped ZnO NP were assigned using the standard JCPDS card No. 36-1451 with phase structures belong to the wurtzite structure with a hexagonal phase and the P63mc space group. The effects of Sm^{3+} concentrations on the crystal and particle size of ZnO NP were investigated. Figure 4.12(a) shows the XRD patterns for the Sm^{3+} -doped ZnO with concentrations ranging from 0.0 to 1.0 wt. % that was calcined at 400°C . The XRD patterns of the dopant samples indicated that doping occurs without any changes in phase structure of the ZnO NP. No peak for samarium oxide (Sm_2O_3) appears on the diffraction spectrum, which conforms that doping occurred in the unit cell of ZnO or that such a low concentration of Sm^{3+} was used is below the detection limit of XRD instrument (Liu et al. 2009). However, when the Sm^{3+} concentration increased, the intensities of the peaks decreased and the peaks became broader compared with the peaks of undoped ZnO.

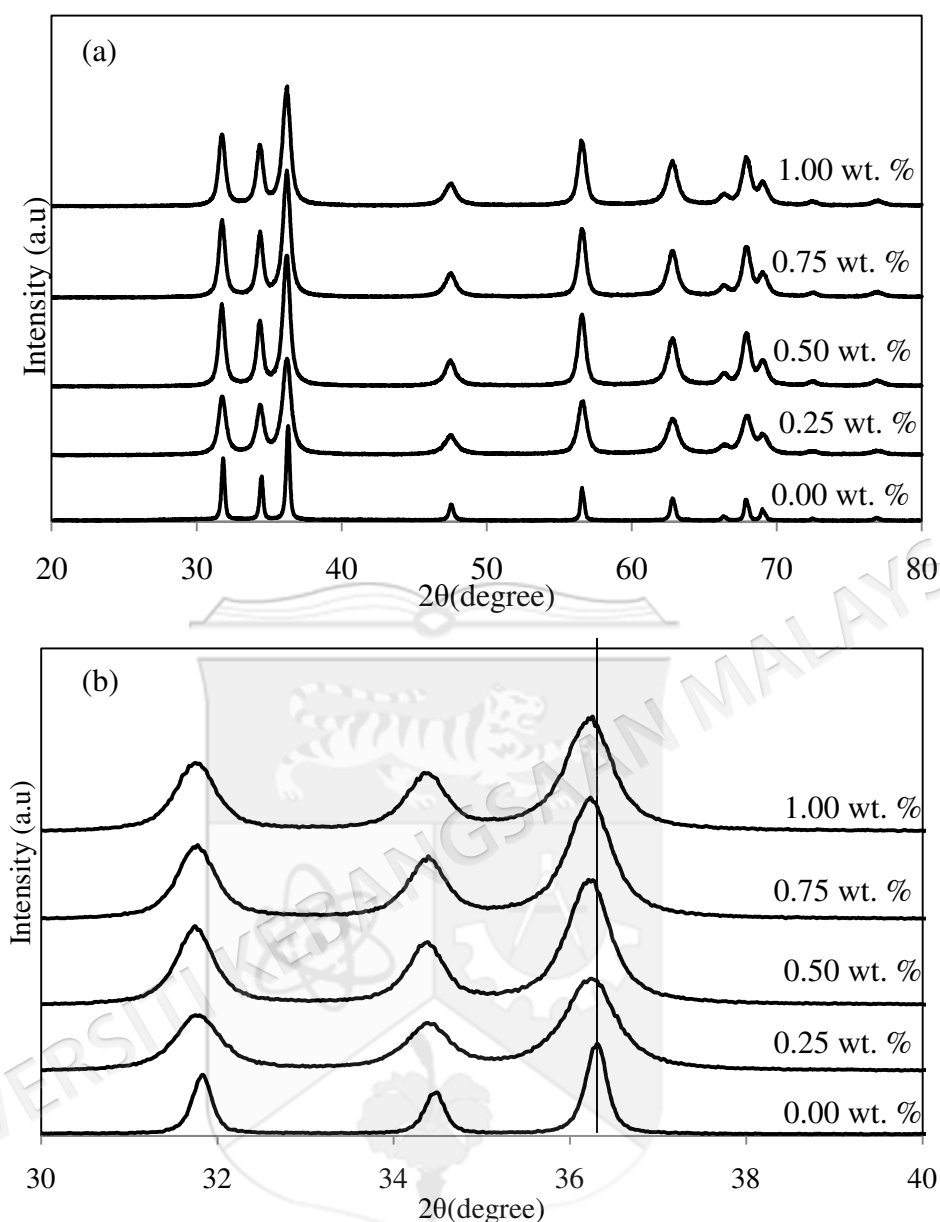


Figure 4.12 XRD patterns spectrum of (a) Sm³⁺-doped ZnO nanoparticles with different concentration calcined at 400°C (b) shifted of peak (101) position is observable towards to left side.

These result confirmed that doping of Sm³⁺ into the ZnO crystal lattice occurred and results of lattices are given in Table 4.8. This phenomenon can be attributed to the differences in the sizes of the ionic radii of the Zn²⁺ (0.074 nm) and Sm³⁺ (0.112 nm) ions (Srivastava et al. 2009). During the doping process, Sm³⁺ easily incorporated with ZnO NP due to the lattice disorder and associated to stresses of ZnO cell as reported in another study (Chen et al. 2008). The doping of Sm³⁺ in lattice of

ZnO was investigated by shifting of peaks (100,002,101) position to left side (lower value of 2θ) with increasing of Sm^{3+} concentration as shown in Figure 4.12 (b). These results showed Sm^{3+} ions substituted Zn^{2+} in matrix of ZnO with caused to increases lattices as reported previously using the ionic radii of dopant lager than Zn^{2+} (Panigrahy et al. 2012).

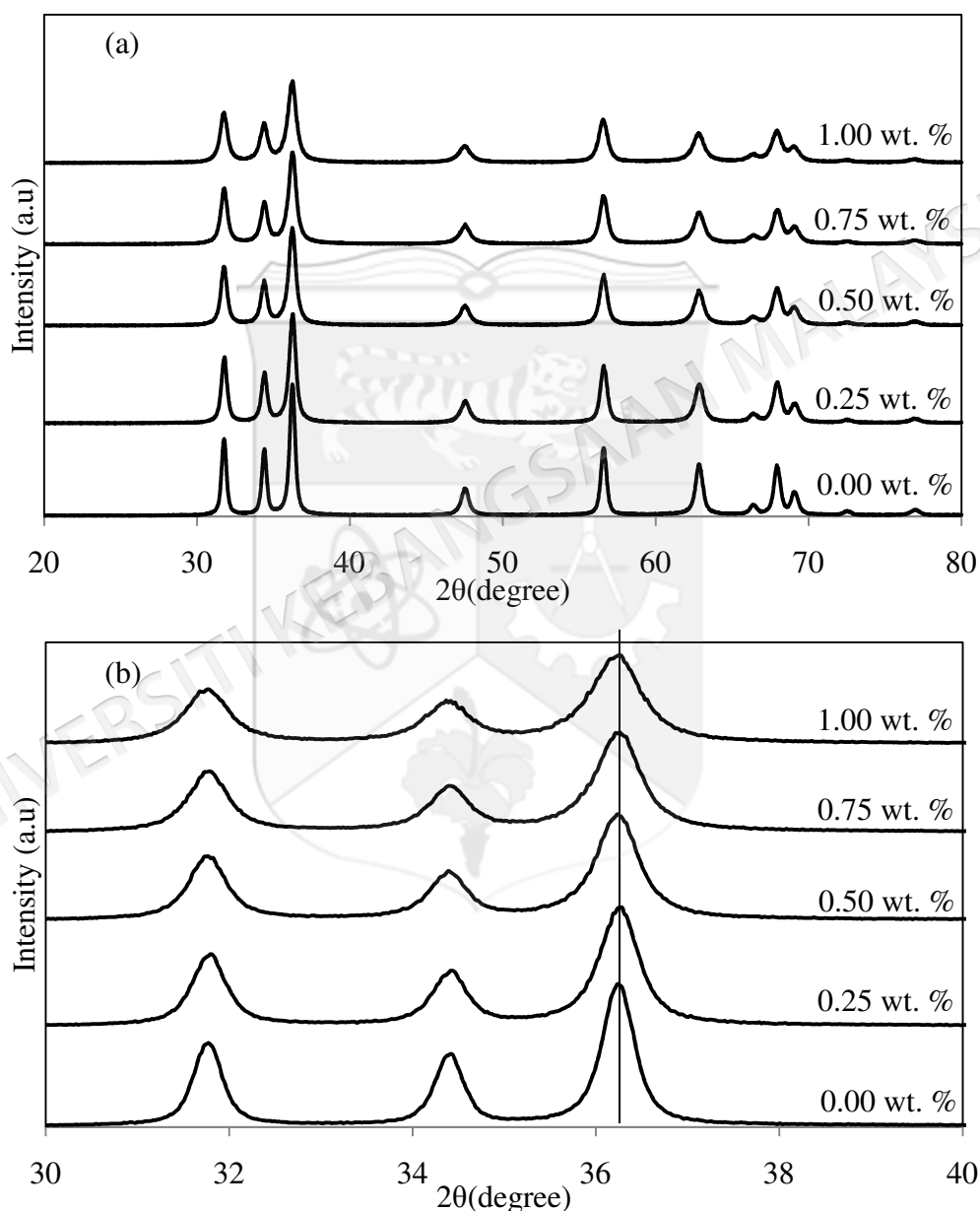


Figure 4.13 XRD patterns of (a) Ti^{4+} -doped ZnO nanoparticles with different concentrations calcined at 400°C (b) no shifting of peak (101) position is observable.

The effect of Ti^{4+} ions doped ZnO NP using same concentration from 0.00 to 1.0 wt. % was investigated also. The XRD patterns of the Ti^{4+} -doped ZnO presents in Figure 4.13 (a) and indicated the structure is wurtzite with a hexagonal phase of ZnO and no peak appeared for any oxide of titanium or Zinc titanate (TiO_2 , ZnTiO_3 , Zn_2TiO_4). The crystal size of Ti^{4+} -doped ZnO was decreased when increase of Ti^{4+} ions concentration from 0.00 to 1.00 wt. %. These results showed that Ti^{4+} ions insert to ZnO matrix by substitution of Zn^{2+} ion with slightly deformation of lattice parameters was occurred (Naeem et al. 2010). Figure 4.13 (b) presented the very slight shifting towards to right (high value of 2θ) due to the ionic radii of Ti^{4+} ions is 0.0683 nm which almost closed to the ionic radii of Zn^{2+} of 0.074 nm (Singh et al. 2009). The same phenomena of decreasing of crystal size with slightly changing on the lattice parameters of TiO_2 when doping by Zn^{2+} into the TiO_2 was observed by other study (Liu et al. 2005). The lattice parameters of all Ti^{4+} -doped ZnO samples are given in Table 4.8. Additionally, the other analysis to confirm that doping process into the ZnO NP such as FESEM, TEM, BET and UV absorbance were used and discussed more details in next section.

Table 4.8 Crystal size and lattice parameters of ZnO and doped ZnO NP with various concentrations of dopants (^a Fe^{3+} , ^b Sm^{3+} , ^c Ti^{4+} -doped ZnO)

Concentration of Dopant (wt. %)	Crystal size (nm)	Lattice parameters a=b	Lattice parameters c
0.00	18.0	0.32490	0.52060
0.25	^a 16.0	^a 0.32490	^a 0.52060
	^b 15.8	^b 0.32501	^b 0.52130
	^c 15.59	^c 0.32490	^c 0.52060
0.5	^a 15.0	^a 0.32488	^a 0.52056
	^b 13.6	^b 0.32501	^b 0.52130
	^c 13.83	^c 0.32501	^c 0.52061
0.75	^a 13.0	^a 0.32480	^a 0.52054
	^b 13.2	^b 0.32530	^b 0.52071
	^c 12.99	^c 0.32488	^c 0.52054
1.00	^a 12.0	^a 0.32488	^a 0.52054
	^b 12.7	^b 0.32530	^b 0.52071
	^c 11.56	^c 0.32480	^c 0.52054

4.5 SURFACE MORPHOLOGY ANALYSIS

The effects of process parameters such as molar ratio, pH and calcination temperatures on the morphology and particle size of ZnO NP was evaluated using the Field Emission Scanning Electron Microscopy (FESEM) with energy-dispersive X-ray spectroscopy (EDX) and Transmission electron microscopy (TEM) with magnification of 75 to 125 K. The optimum conditions of synthesized smaller particle of ZnO NP was selected for doping process by Fe^{3+} , Sm^{3+} and Ti^{4+} ions and the same instrument used to evaluate the influencing of doped ions in morphology of ZnO NP.

4.5.1 Surface Morphology of ZnO NP

The surface morphology of all ZnO NP samples prepared under different experimental conditions was investigated. The effects of these conditions such as the molar ratio of the starting material, the pH of the reactant solution and the calcination temperature on the surface morphology were evaluated. All ZnO NP samples were in spherical shape as shown by the FESEM and TEM images. The high agglomeration of the ZnO NP in the sample that has a molar ratio of 1:1 and 1:3 can be observed in Figure 4.14 (a,a₁ and c,c₁). During the formation of zinc oxalate at the optimum molar ratio of 1:2, each Zn^{2+} ion would undergo chelation with a $\text{C}_2\text{O}_4^{2-}$ ligand to form a stable complex, thus decreasing the aggregation of particles in the nucleation process as can be observed in Figure 4.14 (b,b₁). According to TGA-DSC results, appreciate molar ratio for smaller crystal size was 1:2 and other ratio of 1:1, 1:3 have lower and excess amount of zinc acetate to oxalic acid respectively.

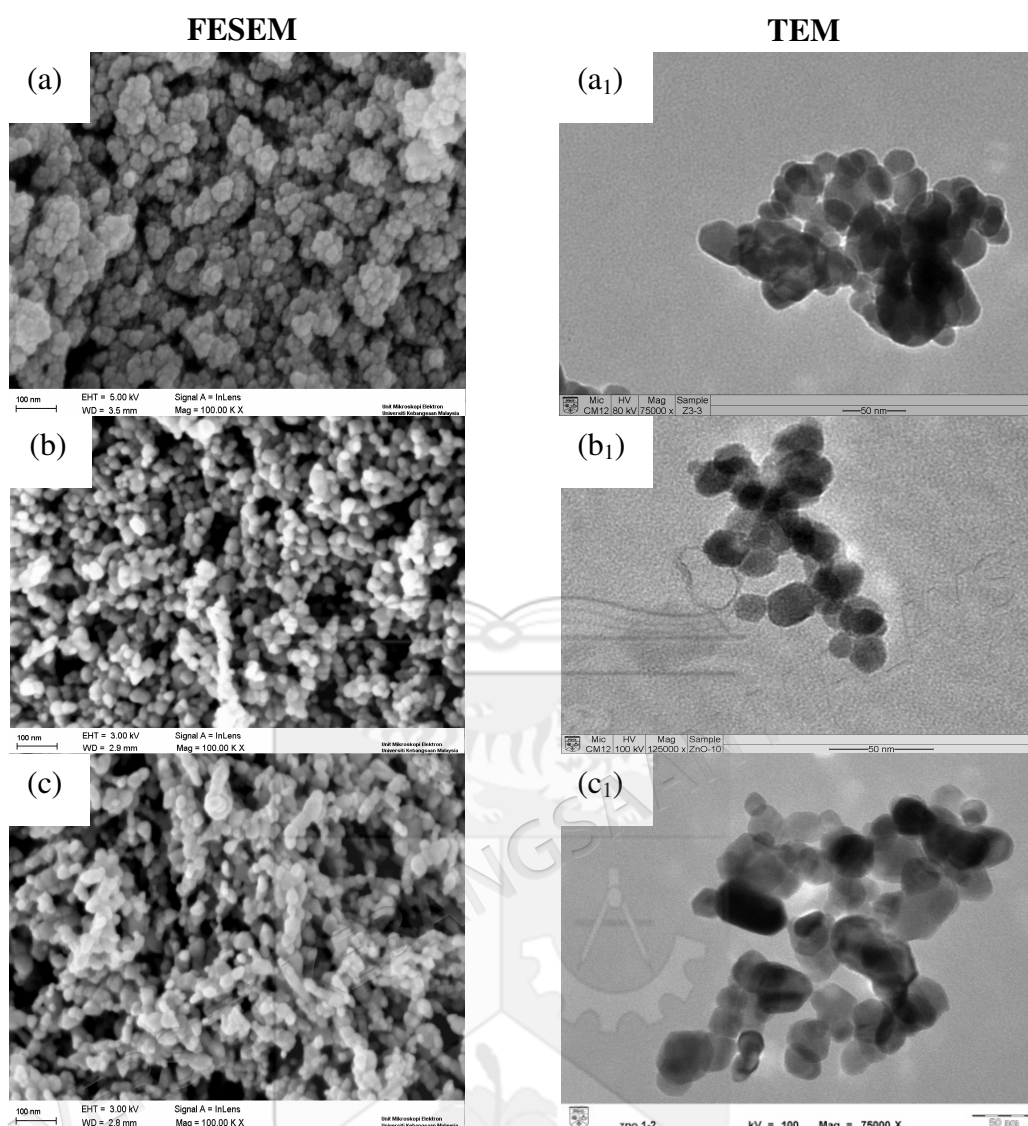


Figure 4.14 FESEM and TEM images of ZnO NP prepared under ratio of Z_{ac}/O_{xa} , (a,a₁) 1:1, (b,b₁) 1:2, (c,c₁) 1:3.

At same time, higher or lower $C_2O_4^{2-}$ ions than the suitable amount (optimum) resulted an inhibition through of hydrolysis and polycondensation process leading to agglomeration of the small particles (Wahab et al. 2009). The ratio less or more than optimal was influenced on size of final particle of ZnO NP as reported by previous studies (Nejati et al. 2011). The TEM images were investigated of ZnO sizes with clearly affecting of the synthesis process factors as summarized in Table 4.9.

Table 4.9 Comparison of particle size between TEM and XRD under different experimental conditions

NO	Molar ratio	pH ± 0.2	Calcination Temperature $^{\circ}\text{C}$	Crystal size by XRD (nm) ± 2	Particle size TEM (nm) ± 2
1	1:1	2	400	30	32
2	1:2	2	400	18	20
3	1:3	2	400	35	37
4	1:2	1	400(without wash)	70	58
5	1:2	1	400(with wash)	30	34
6	1:2	3	400	32	34
7	1:2	5	400	28	30
8	1:2	2	400	18	20
9	1:2	2	500	27	29
10	1:2	2	600	35	38

Figure 4.15 shows the clear effects of pH on ZnO NP size and morphology under various pH values of 1.0 to 5.0 ± 0.2 . At lower pH of 1.0 ± 0.2 indicates bigger size with higher agglomeration was observed. These results may be attributed to adjusted pH by HCl which of H^+ ions that affects on hydrolysis and condensation reaction by limitation number ZnO nuclei in solution which form the bigger particle (Sunandan & Dutta 2009). Figure 4.15 (a_{2,3} & b_{2,3}) shows the size and agglomeration of particle under pH of 1.0 ± 0.2 before and after washing four times by water and one time by ethanol. Bigger size with significant agglomeration was observed of sample before washing which reflects of H^+ presence on sample that could result attractive with $\text{C}_2\text{O}_4^{2-}$ to inhibition of growth of the ZnO within the heat treatment. This observation was confirmed by the TGA-DSC analysis with shifting of final decomposition temperature from 400 to 480 $^{\circ}\text{C}$. After washing, the size was decreased with lower agglomeration than before washing was observed. This phenomenon indicates that almost all acid was removed by indication of water pH after washing. At same time, the TGA-DSC analysis after washing was almost closed to theoretical results at 400 $^{\circ}\text{C}$ as shown in Figure 5.1 (b). When the pH at 2 ± 0.2 , the particle showed smaller with less agglomeration which attributed to grow the particle faster enough of starting martial of molar ratio 1:2 with avoid of additive affects as shown in Figure 4.15 (c_{2,3}). The acidic route has been reported as appreciate solution under optimum value of pH for synthesized smaller particle of ZnO NP (Zhang et al. 2009).

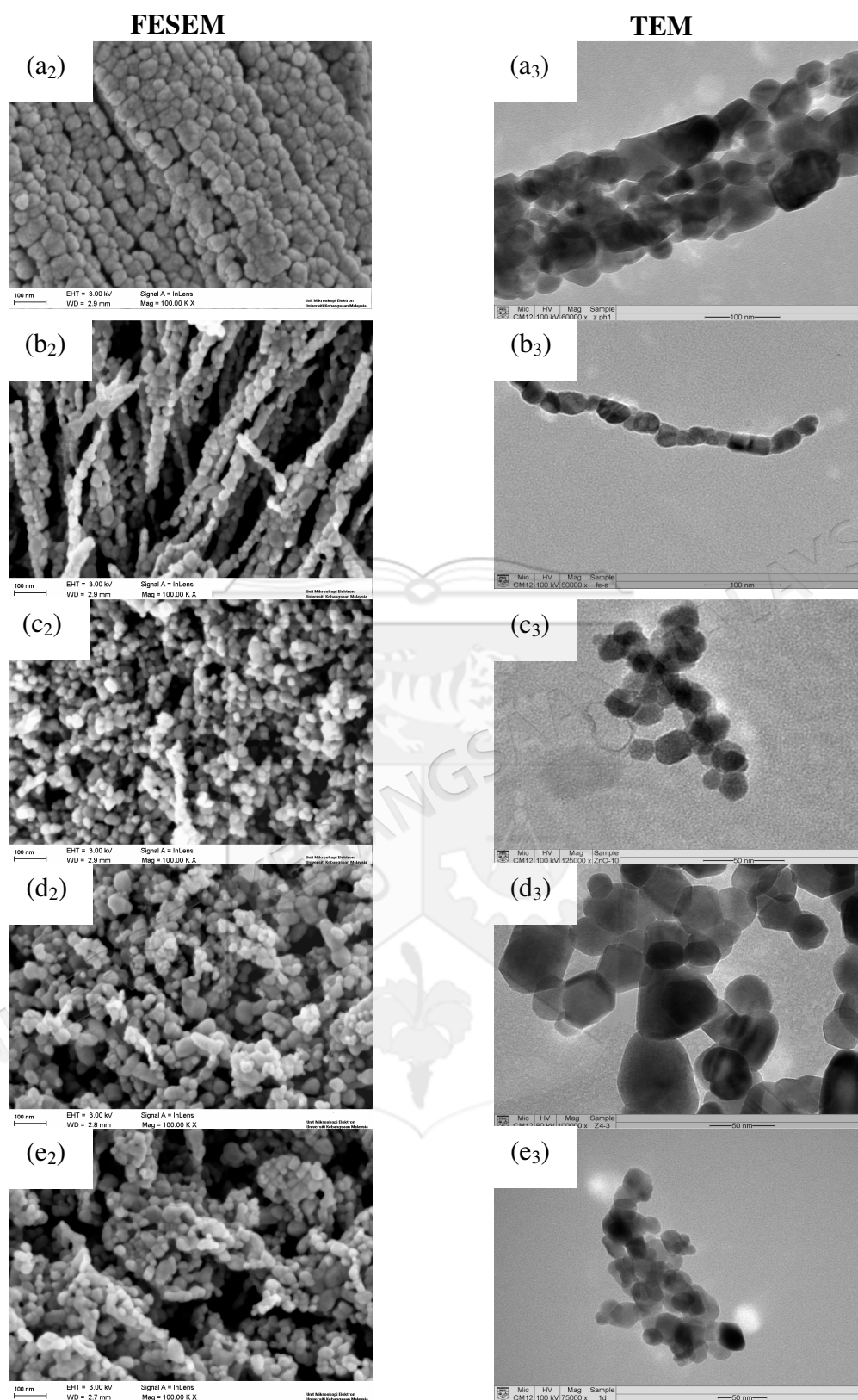


Figure 4.15 FESEM and TEM images of ZnO NP prepared under 1:2 molar ratio and various of pH at (a₂,a₃) 1.0 before washing; (b₂,b₃); 1.0 after washing; (c₂,c₃) 2.0; (d₂,d₃) 3.0; (e₂,e₃) 5.0 ± 0.2.

Through the adjustment of the reactant pH value at 3.0 using ammonia, the NH_4OH molecules were able to interact between two Zn^{2+} ions to produce a three-dimensional complex. However, this process is known to inhibit the complete of the Zn^{2+} ion reacted with the $\text{C}_2\text{O}_4^{2-}$ ions. Thus reaction (hydrolysis and condensation) was become slower which was leading to the formation of large irregular nanoparticles with less agglomeration as shown in Figure 4.15 (d_{2,3}). However, at pH 5.0 shown in Figure 4.15 (e_{2,3}), the size of particle decreased may due to more amount resulted in the formation of stable Zn^{2+} complex with ammonia which helps the growth of the ZnO particle faster with agglomeration of particle each other (Yu et al. 2007). The results obtained from the analysis TEM were in good agreement with crystal size measured by XRD, the values given in Table 4.9.

The effect of calcination temperatures on particle size with maintaining the other experimental conditions optimal at 1:2 molar ratio and pH of 2.0 ± 0.2 is given in Figure 4.16. It was observed that a linear relationship between the calcination temperatures and particle size. The size of particle was become bigger with temperatures increasing from 400 to 600 °C and values were given in Table 5.3. These results indicate that increasing in particle size were mainly due to the crystal growth at temperatures beyond 400°C (Chen et al. 2009). Additionally, the agglomeration of small particles under higher temperature leads to growth particle as reported by previous study (Seetawan et al. 2011). Moreover, XRD results were in the same trend of calcination temperature affect on size, which shows higher crystallinity (shaper peak) indicting a bigger particle.

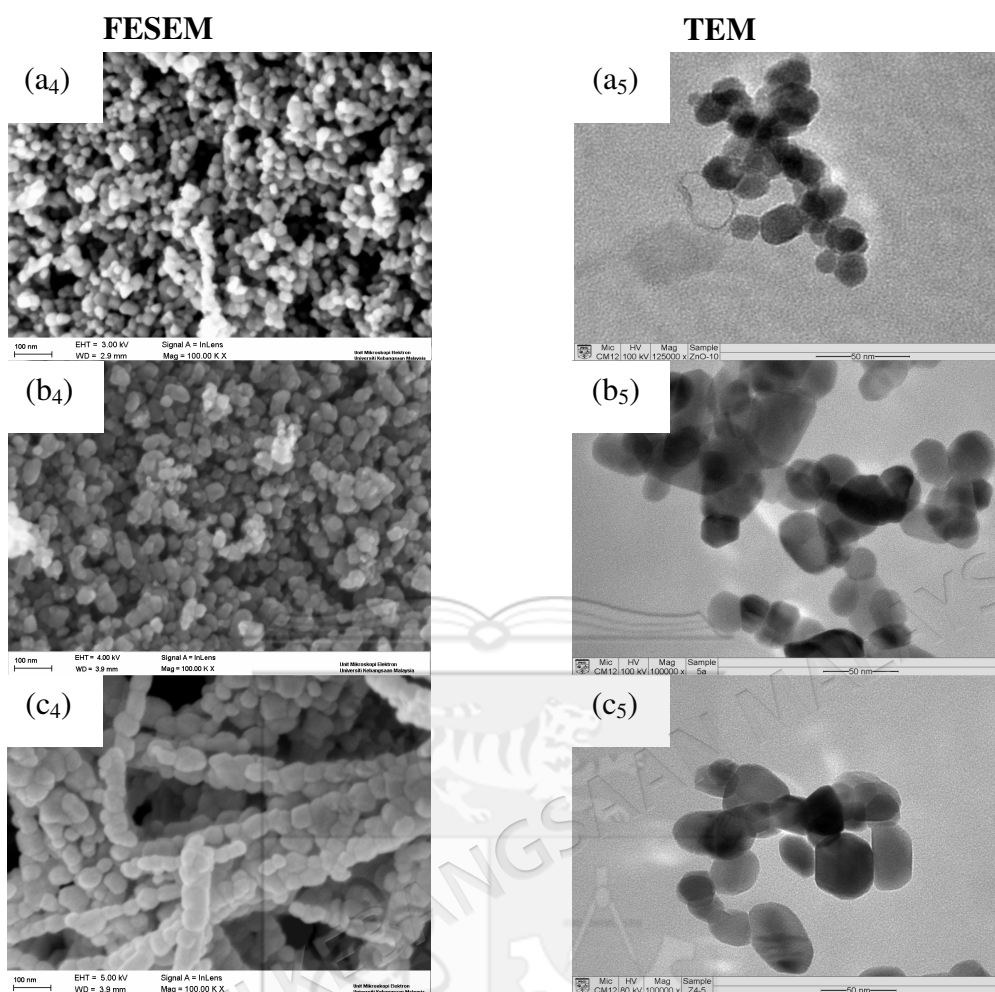


Figure 4.16 FESEM and TEM images of ZnO NP prepared under 1:2 molar ratio and pH of 2.0 at calcination temperature of (a₄,a₅) 400°C, (b₄,b₅) 500°C, (c₄,c₅) 600°C.

The final composition of ZnO NP with several molar ratio, pH and calcination at different temperatures were analyzed using EDX. Only Zn and O were detected through EDX analysis, which confirmed that ZnO was the final product without any other impurities as shown in Figure 4.17. The atomic percentage of Zn and O was found to be at an approximate stoichiometric ratio of 1:1 as presented in Table 4.10.

All results in this study have shown that the optimization of the parameters to control the particle size is the significant step for ZnO NP synthesis with no addition of any surfactant and capping agents. The size of ZnO NP produced by sol gel method in presence of capping agents without optimizing the process parameters showed particle size higher than was achieved in this study.

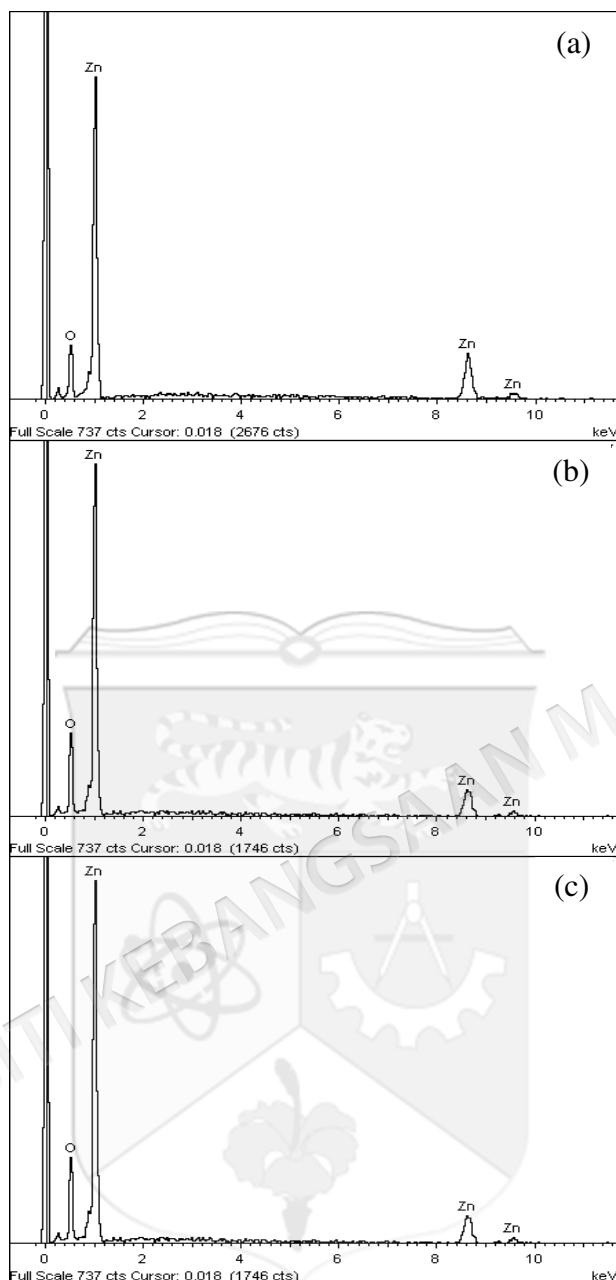


Figure 4.17 EDX of ZnO NP calcined at 400°C with various values of pH, (a) 2.0, (b) 3.0, (c) 5.0±0.2.

On the other hand, particle size of ZnO higher than 42 and 47 nm were produced by the precipitation method without optimization of parameters and any capping agents added (Hayat et al. 2011; Goswami & Sharma 2010). Other techniques for ZnO NP synthesis using the direct thermal and mechano-chemical also produce higher ZnO particle size of 32 and 50 nm have been reported by an earlier study (Labuayai et al. 2009).

Table 4.10 The weight % and atomic % results of ZnO nanoparticle at different conditions

Molar ratio	pH ± 0.2	Calcination Temperature °C	O K		Zn L	
			Wt %	At %	Wt %	At %
1:1	2	400	16.96	45.50	83.04	54.50
1:2	2	400	17.87	47.06	82.13	52.94
1:3	2	400	19.96	50.47	80.04	49.53
1:2	3	400	16.96	45.50	83.04	54.50
1:2	5	400	18.96	48.87	81.04	51.13
1:2	2	400	17.87	47.06	82.13	52.94
1:2	2	500	20.19	50.82	79.81	49.18
1:2	2	600	22.39	54.10	77.61	45.90

K and L: orbitals of oxygen and zinc

4.5.2 Surface Morphology of Doped ZnO NP

Generally, doping of semiconductor has many advantages for controlling the size, shape and surface of nanoparticles which could be improved those materials for many applications. In order to synthesize a useful doping particle one needs to know the compatibility of doped and host element. The doping ZnO NP by transition metals shows good results for application especially when using the zinc acetate as precursor material of ZnO and organic solvent. In this study, the Fe^{3+} , Sm^{3+} and Ti^{4+} ions were selected to enhance ZnO properties in which prepared by sol gel method. These dopants have lack of detail in the aspect of application listed in Table 2.4. However, the Ti^{4+} doped ZnO NP (spherical) as powder only reported recently by Tseng et al. (2012) with no further details on application. The morphology of Fe^{3+} , Sm^{3+} and Ti^{4+} doped ZnO NP were investigated using FESEM and TEM with magnification of 100 to 340 K and compared with undoped ZnO NP. ZnO and doped ZnO NPs were prepared under same experimental condition of molar ratio of 1:2, pH at 2.0 ± 0.2 and calcinations temperature at 400°C . Various concentrations of Fe^{3+} , Sm^{3+} and Ti^{4+} ions between 0.00 to 1.0 wt. % of each Zn^{2+} were used to study the effects of dopant on the morphology and particle size of ZnO NP.

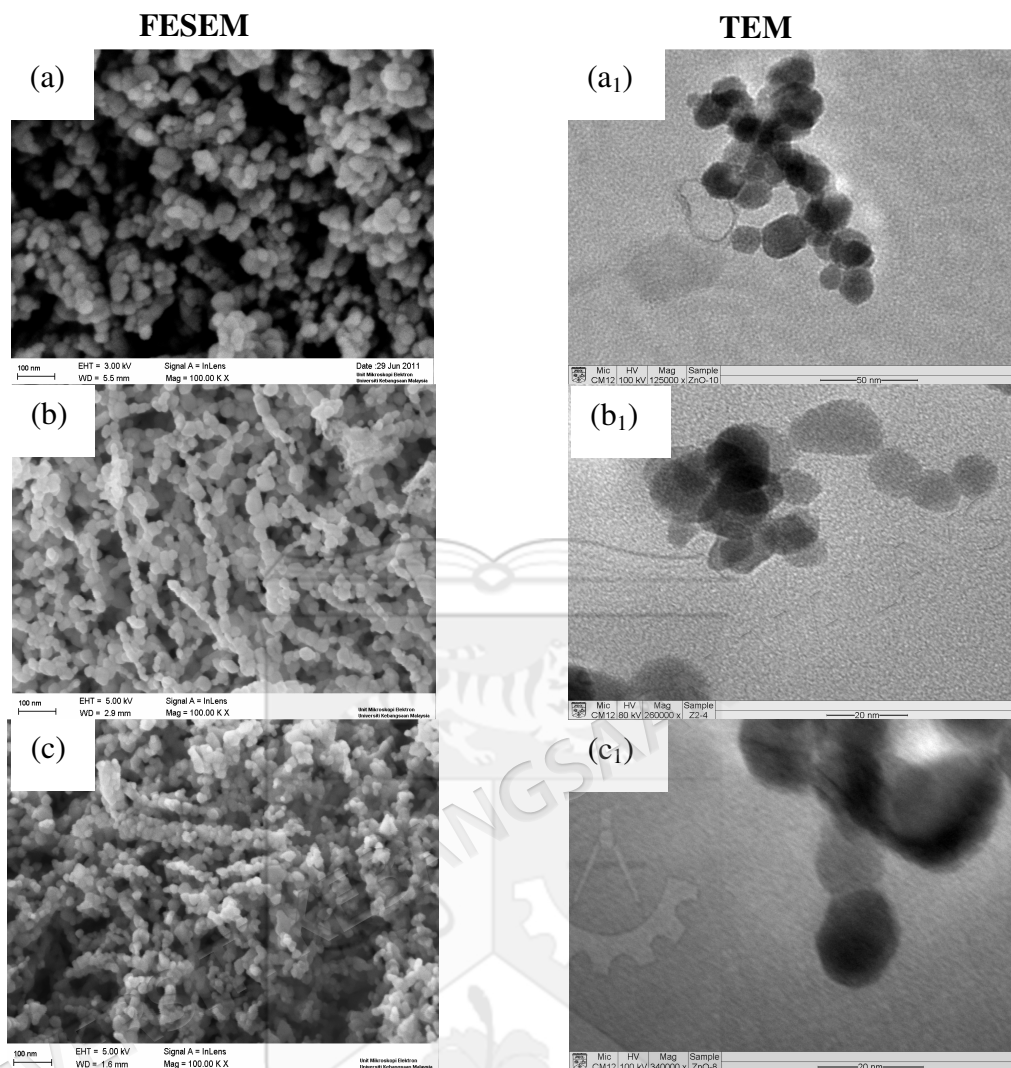


Figure 4.18 FESEM and TEM images of (a, a₁) undoped ZnO NP; (b, b₁) 0.5 wt. % of Fe³⁺; (c, c₁) 1.00 wt. % of Fe³⁺ doped ZnO NP.

The images of FESEM and TEM reveal that for ZnO and Fe³⁺, Sm³⁺ and Ti⁴⁺ doped ZnO, the particles were mostly spherical in shape. However, the significant aggregation of undoped ZnO particle each other was observed by FESEM images using high magnification compared doped ZnO samples. The aggregation between the particles decreases for doped ZnO NP with the concentration when increased from 0.00 to 1.0 wt. %. For study of influences of doping on ZnO morphology FESEM and TEM, the middle and higher concentration samples were selected for more clear of FESEM and TEM showing results.

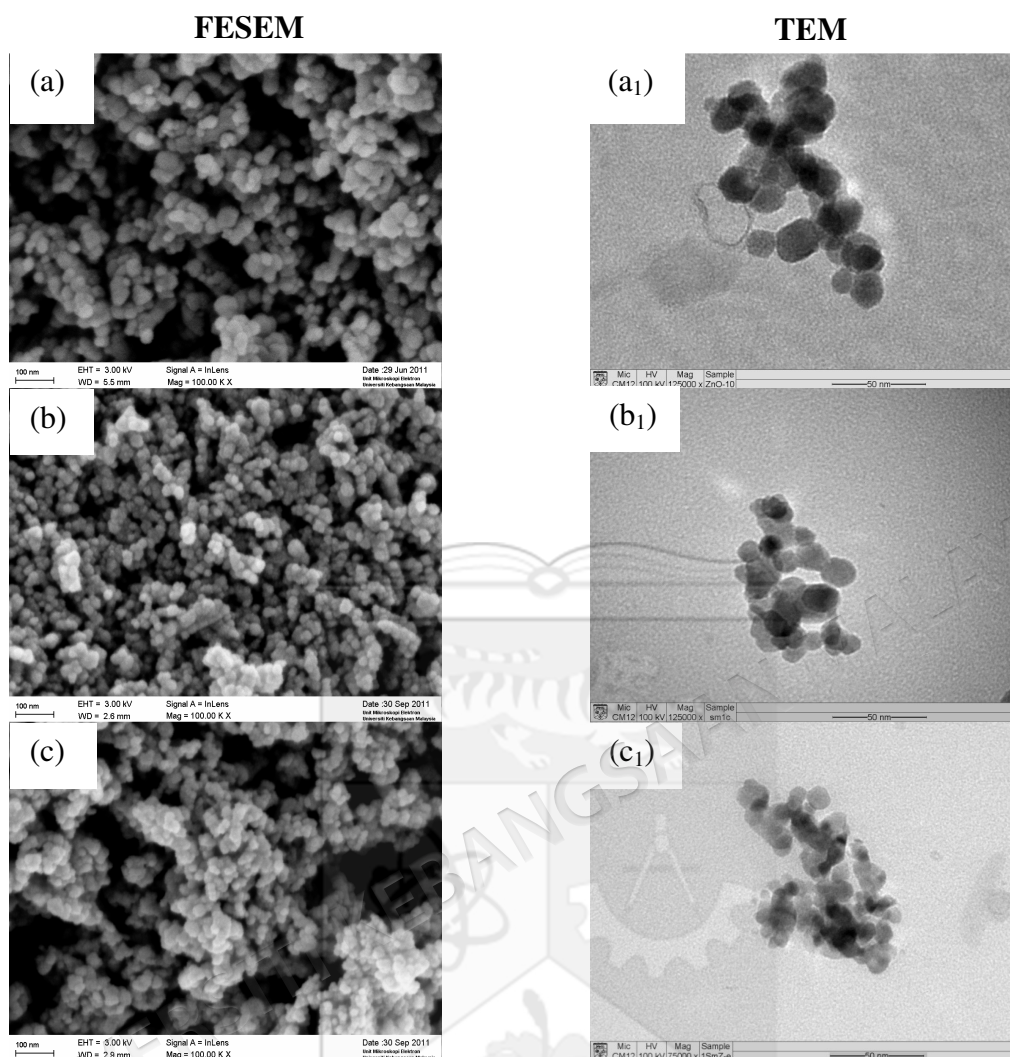


Figure 4.19 FESEM and TEM images of (a, a₁) undoped ZnO; (b, b₁) 0.5 wt. % of Sm³⁺; (c, c₁) 1.00 wt. % of Sm³⁺ doped ZnO.

Moreover, these samples reflect the highest activity for application as solar photocatalyst. All doped ZnO NP by Fe³⁺, Sm³⁺ and Ti⁴⁺ with concentrations of 0.5 and 1.00 wt.% exhibit that aggregation was became less compared the undoped with uniform of particle size and spherical shape as shown in Figure 4.18, 4.19 and 4.20, respectively.

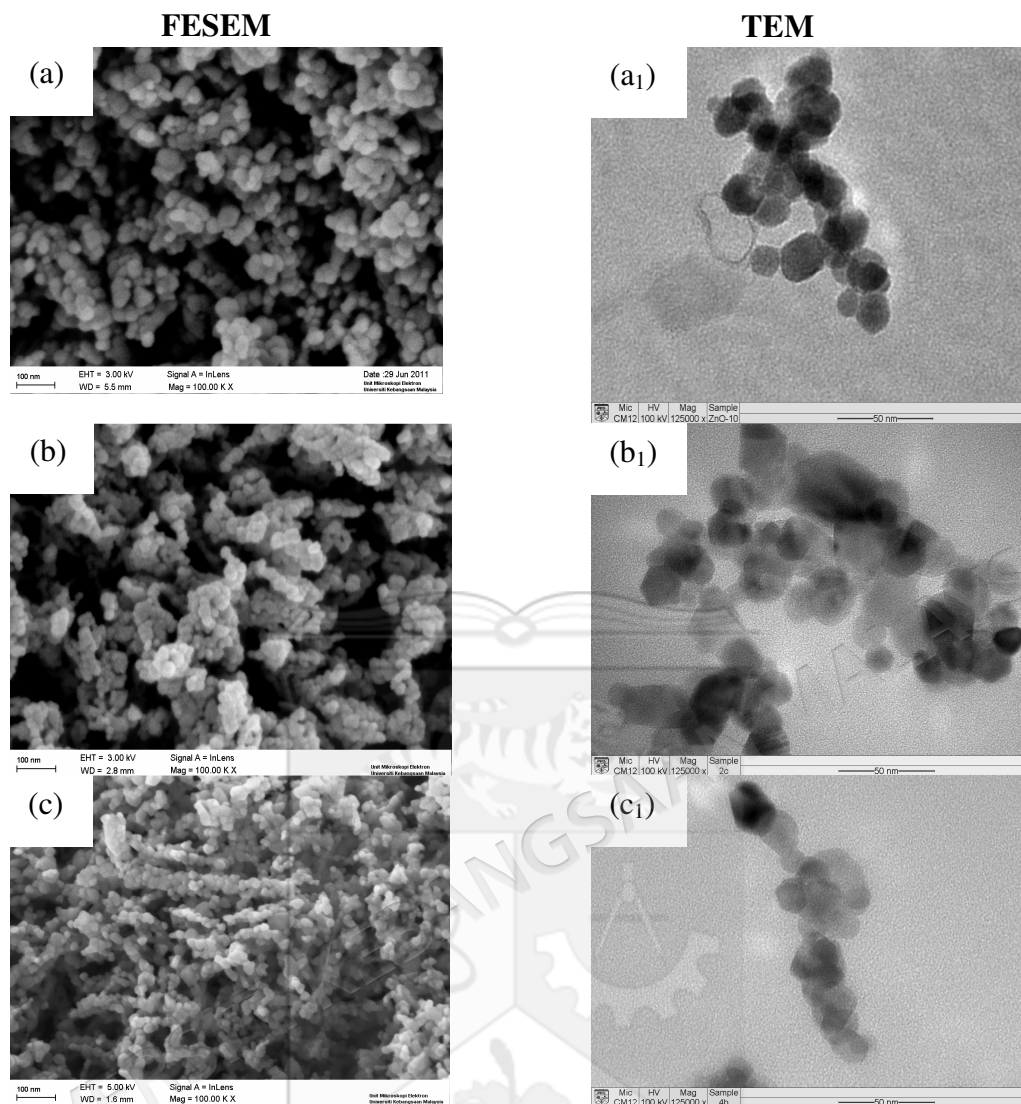


Figure 4.20 FESEM and TEM images of (a, a₁) undoped ZnO; (b, b₁) 0.5 wt.% of Ti⁴⁺; (c, c₁) 1.00 wt.% of Ti⁴⁺ doped ZnO.

As shown in TEM images in Figure 4.18, Figure 4.19 & Figure 4.20, respectively which is very clear the particle size of the Fe³⁺, Sm³⁺ and Ti⁴⁺ doped ZnO samples decreases as the concentration of ions increased. The particles of ZnO and doped ZnO NP are in spherical shape with uniform distribution of size. Upon further increase of the concentration from 0.00 to 1.00 wt. %, the average particle size decreases from 20 and 11±2 nm, respectively, this is consistent with the results obtained from XRD data. Additionally, the slight agglomeration of Sm³⁺ and Ti⁴⁺ doped ZnO samples were observed when concentration increased from 0.50 to 1.00 wt. % which attributed to the aggregates of small particles formed after doping

process as reported by the Tseng et al. (2012). The TEM results prove that Fe^{3+} , Sm^{3+} and Ti^{4+} successfully doped into ZnO NP which confirmed by inhibition of the peak crystallization and shifting of position on XRD analysis. The doping of ZnO by Fe^{3+} , Sm^{3+} and Ti^{4+} caused the changes in the interplanar spacing which lead to shifting the diffraction angle to lower or higher value was observed.

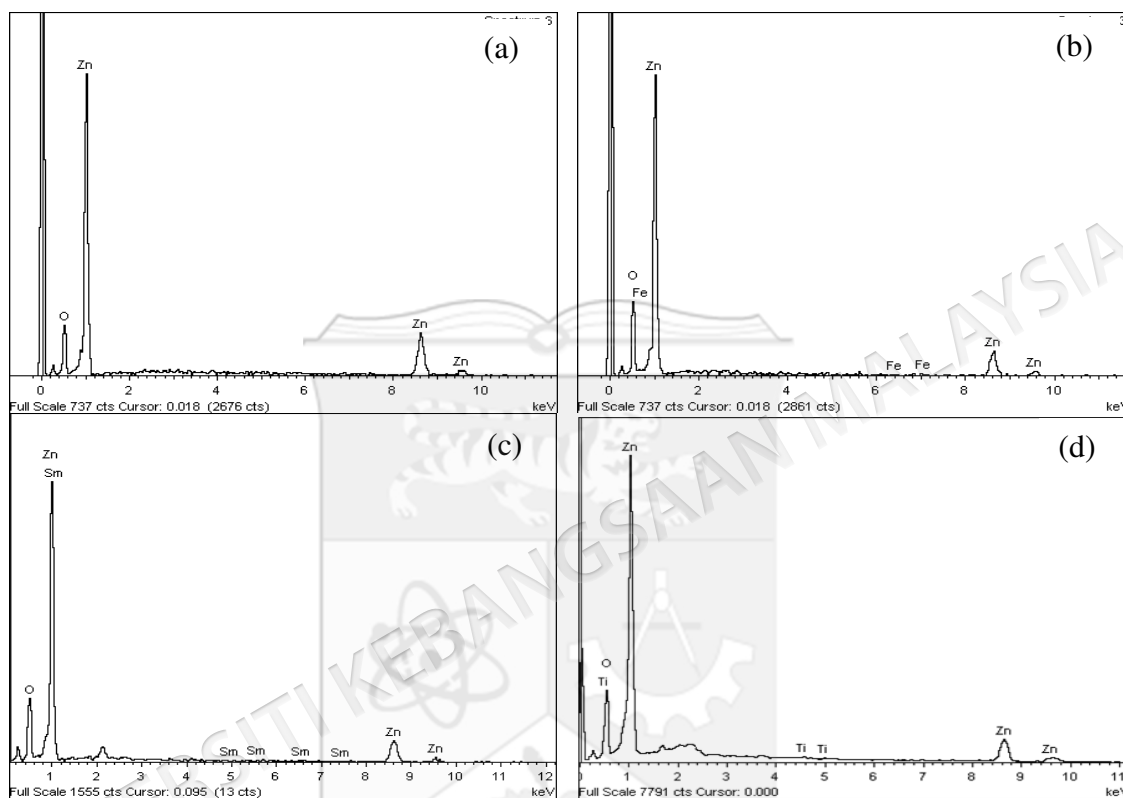


Figure 4.21 Energy dispersive X-ray (EDX) of different dopant into ZnO (a) undoped ZnO; (b) Fe^{3+} ; (c) Sm^{3+} ; (d) Ti^{4+} .

The real concentration of Fe^{3+} , Sm^{3+} and Ti^{4+} ions cooperates of ZnO after the calcination stage was estimated by energy dispersive X-ray (EDX) and given in Figure 4.21. The EDX analysis confirms that doped of ions into the host structure of ZnO was succeeded and dopant detecting as wt. % and summarized for middle and high concentration in Table 4.11. The oxygen value of doped samples showed slightly more than undoped ZnO which attributed that dopant by high valance such as Fe^{3+} , Sm^{3+} and Ti^{4+} and substitution of Zn^{2+} in the host of ZnO have been reported (Pala & Metiu, 2007). These results also shows that Zn, O and Fe^{3+} , Sm^{3+} and Ti^{4+} only

presence without any impurities which in good agreement with XRD that exhibited successfully doping in the matrix of ZnO NP.

Table 4.11 The weight % and atomic % results of doped ZnO NP at optimum concentration.

Dopant type	Element	Wt %	At %
Pure	O K	19.91	50.39
	Z L	80.09	49.61
Fe ³⁺	Fe K	0.47	0.17
	O K	21.83	53.35
	Z L	77.70	46.48
Sm ³⁺	Sm K	0.48	0.39
	O K	20.77	51.54
	Z L	78.75	48.07
Ti ⁴⁺	Ti K	0.49	0.40
	O K	21.89	53.32
	Z L	77.62	46.28

K and L: orbital of oxygen, iron, samarium, titanium and zinc

4.6 OPTICAL PROPERTIES

Optical properties of semiconductor are the one of very important properties for many applications focused within last few years. ZnO NP has the optical properties in near UV and visible regions which can be used in a variety of applications such as ultraviolet lasers and diodes, piezoelectric devices and photocatalysts. Different of ZnO NP shape and morphologies affect on optical properties which could determine the specific application such as the fine ZnO NP properties (band gap) are suitable for using as UV detectors and emitters. The optical properties such as band gap (reflectance and absorbance) of ZnO and doped ZnO NP were determined using UV spectrophotometers. Effects of the process parameters such as molar ratio, pH and calcination temperatures on the optical properties of ZnO NP were reported in this section. Additionally, the improvement of optical properties for ZnO NP by doping of Fe³⁺, Sm³⁺ and Ti⁴⁺ ions were also summarized.

4.6.1 Optical Properties of ZnO NP

The optical properties of ZnO NP prepared by sol gel under different process parameters of molar ratio, pH of solution and calcination temperatures were

investigated in details of diffuse reflectance and absorbance spectroscopy. An effect of molar ratio was evaluated under ratio of zinc acetate at one mole to oxalic acid from 1 to 3 with pH at 2.0 ± 0.2 and temperature of $400\text{ }^{\circ}\text{C}$. Figure 4.22 shows the steps to calculate the band gaps which determine the reflectance and absorbance were firstly determined and then band gap was calculated according the equation below:

$$\alpha h\nu = E_d (h\nu - E_g)^{\frac{1}{2}} \quad (4.7)$$

where α is the optical absorption coefficient, $h\nu$ is the photon energy, E_g is the direct band gap, and E_d is constant (Sarawuth et al. 2009). By plotting $(\alpha h\nu)^2$ as a function of photon energy and extrapolating the linear portion of the curve to a value of zero, the value of the band gap (E_g) of ZnO NP can be obtained at different conditions.

The lower diffuse reflectance of ZnO NP under different molar ratio indicates the higher absorption under same wavelength region in between of 200 to 600 nm as shown in Figure 4.22 (a,b). Figure 4.22 (c) shows that energy band gap values were increased from 3.05 to 3.198 eV with the molar ratio increasing from 1 to 3. These results indicate that molar ratio has influenced on ZnO morphology and particle size which lower ratio leads to bigger size growth that were confirmed by FESEM and TEM images. However the best results of band gap was 3.198 eV which found under molar ratio of 1:2 as the optimal ratio to produce the lower size of particle and reported by XRD, FESEM and TEM results. Furthermore, molar ratio of 1:2 and 1:3 indicates that energy of band gap of 3.198 and 3.115 eV respectively which is good because less agglomeration of particles was observed in TEM results than 1:1.

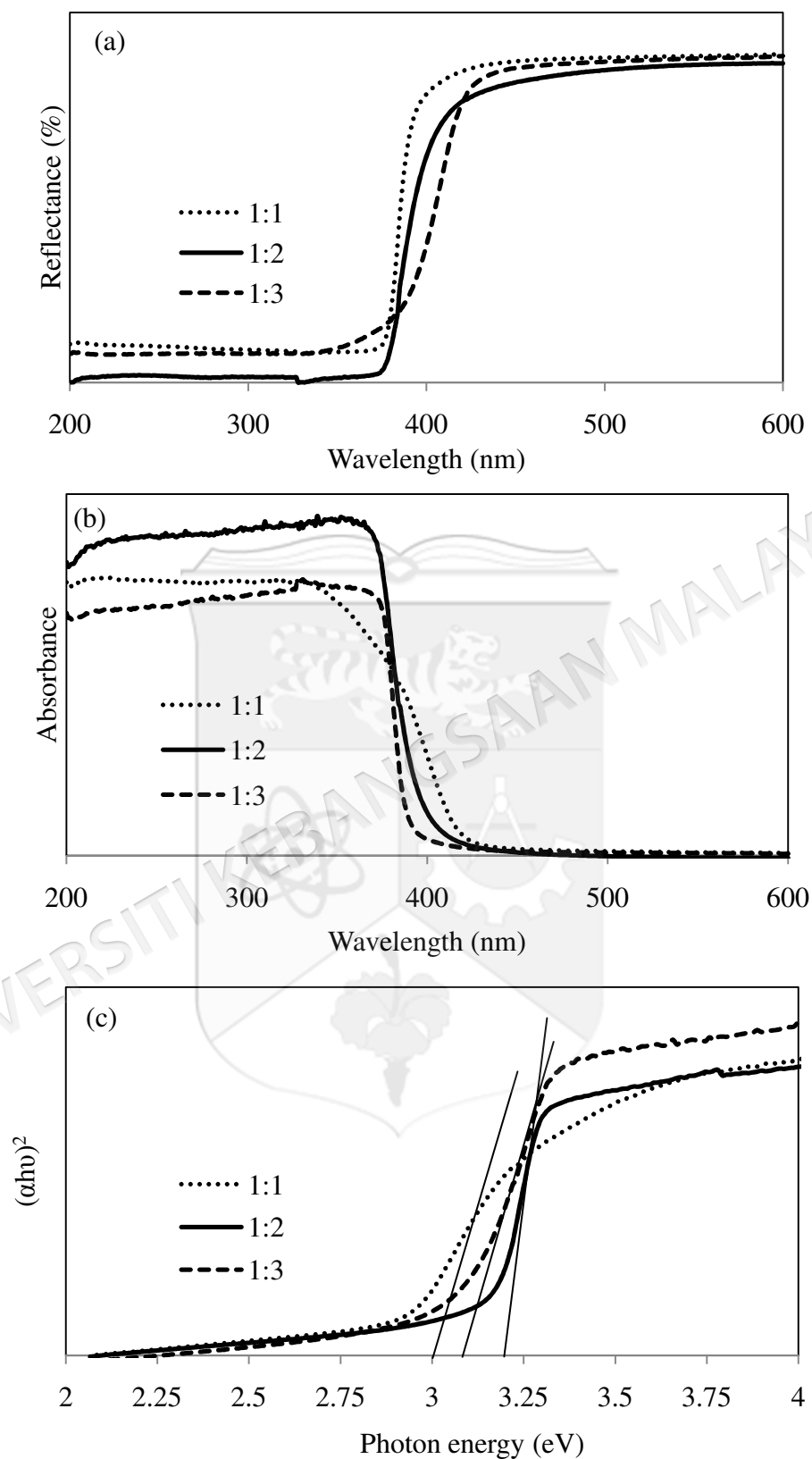


Figure 4.22 Optical properties of ZnO NP under different molar ratio (a) Diffuse Reflectance, (b) Absorbance, (c) Band gap.

Effects of pH and calcination temperatures on the optical properties of ZnO NP were investigated and shown in Figure 4.23. After the gel was dried at 80°C, zinc oxalate was obtained as a precursor powder of the ZnO NP. Zinc oxalate shows no absorbance within the UV region which indicated there no band gap for zinc oxalate and could not be used as photocatalyst as given in Figure 4.23 (a). The heat treatment was enhanced of the optical absorbance of zinc oxalate by converting to oxide as ZnO at temperature of 400 °C according to TGA-DSC analysis.

Effects of calcination temperatures on optical properties (band gap) of ZnO NP were evaluated and given in Table 4.12. The variations of band gaps were found to be in decreases with calcination temperatures increase from 400 to 600°C. This variation results by the strain of particles which lead to change in size, in which confirmed by the XRD patterns data. when calcintion temperatures increases, the absorption at range of wavelength less than 400 nm was increased because the transition of electron from the valance band to the conduction band (O_{2p} to Zn_{3d}) which call it intrinsic band gap (Sarawuth et al. 2009).

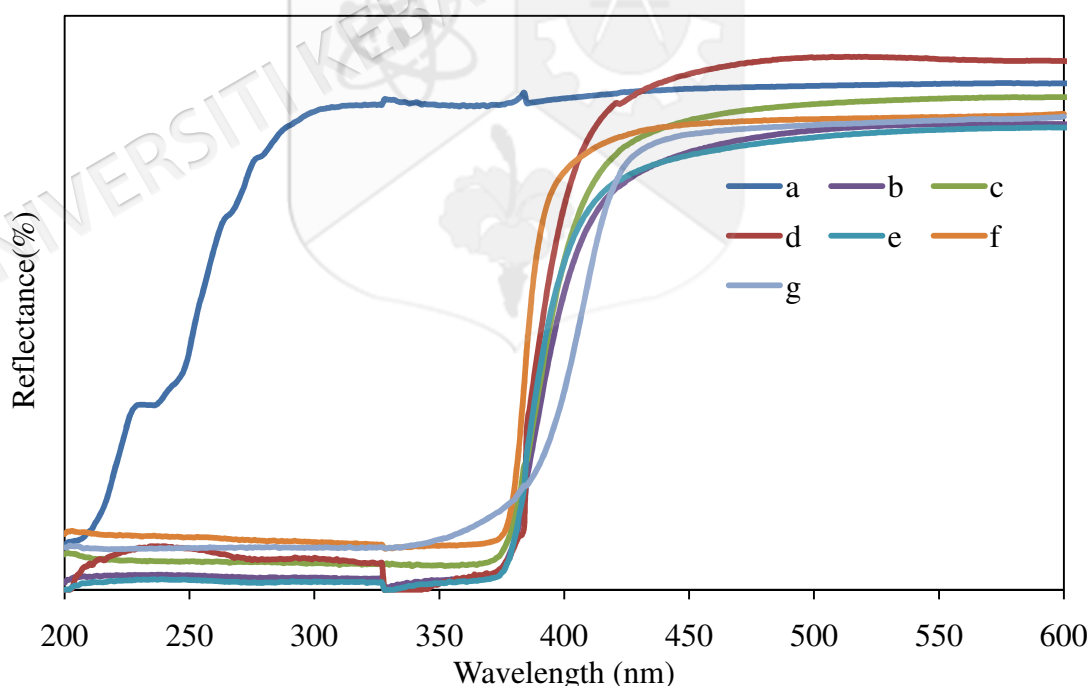


Figure 4.23 Diffuse reflectance of the ZnO precursor (a) before calcinations; (b) at 400°C; (c) 500°C; (d) 600°C; (e) ZnO commercial; (f) at pH of 3.0; (g) at pH of 5.0.

The band gap of synthesized ZnO NP at different pH values from 2.0 to 5.0 ± 0.2 decreased as the pH increased as given in Table 4.12. The absorption of the ZnO NP has been strongly affected by the particle sizes, which could influence the ability of the ZnO NP to absorb UV light (Hung & Whang 2003). The band gap of ZnO NP was reported to be similar as in other previous studies (Sarawuth et al. 2009). The change in the value of the band gap was observed to have been attributed to the effects of the ZnO particle size (Hung & Whang 2003). For most applications of ZnO NP, the suitable band gap can be estimated to be between 3.0 to 3.4 eV at room temperature (Pearton et al. 2005).

Table 4.12 Optical properties of ZnO nanoparticles under different conditions

Sample No	Molar ratio	pH of sample	Calcination Temperature (°C)	Band gap (eV)
1	1:1	2.0 $\pm$ 0.2	400	3.05 $\pm$ 0.02
1	1:2	2.0 $\pm$ 0.2	400	3.198 $\pm$ 0.02
1	1:3	2.0 $\pm$ 0.2	400	3.115 $\pm$ 0.02
2	1:2	2.0 $\pm$ 0.2	500	3.163 $\pm$ 0.02
3	1:2	2.0 $\pm$ 0.2	600	3.112 $\pm$ 0.02
4	1:2	3.0 $\pm$ 0.2	400	3.108 $\pm$ 0.02
5	1:2	5.0 $\pm$ 0.2	400	3.132 $\pm$ 0.02

The effects of the particle size on the absorption spectra which that produced under different of process parameters was investigated by UV-vis spectrophotometer as shown in Figure 4.24. Every sample run shows one peak of spectrum confirms that the pure ZnO NP with size chang. The sharpness peak of UV absorption was observed of sample under 1:2 with cut off absorption at 375 nm as shown in Figure 4.24 (a). The shifting of the absorption spectrum of 1:1 and 1:3 to red shift (higher wavelength) was corresponding to the results from increasing the size of ZnO NP and blue shifting (lower wavelength) indicates that size of the ZnO decreased at 1:2 which have been reported previously (Wahab et al. 2009). However, the red shift of absorption peaks (more than 375 nm) were occurred for calcination temperature of ZnO NP more than 400°C and pH more than 2.0 $\pm$ 0.2 as given in Figure 4.24 (b). The shifting of peaks to red region with decrease of intensity was attributed to the change of morphology (particle size) and optical band gap of ZnO NP under several of experimental conditions. These results in good agreement with that estimated using XRD results for ZnO NP.

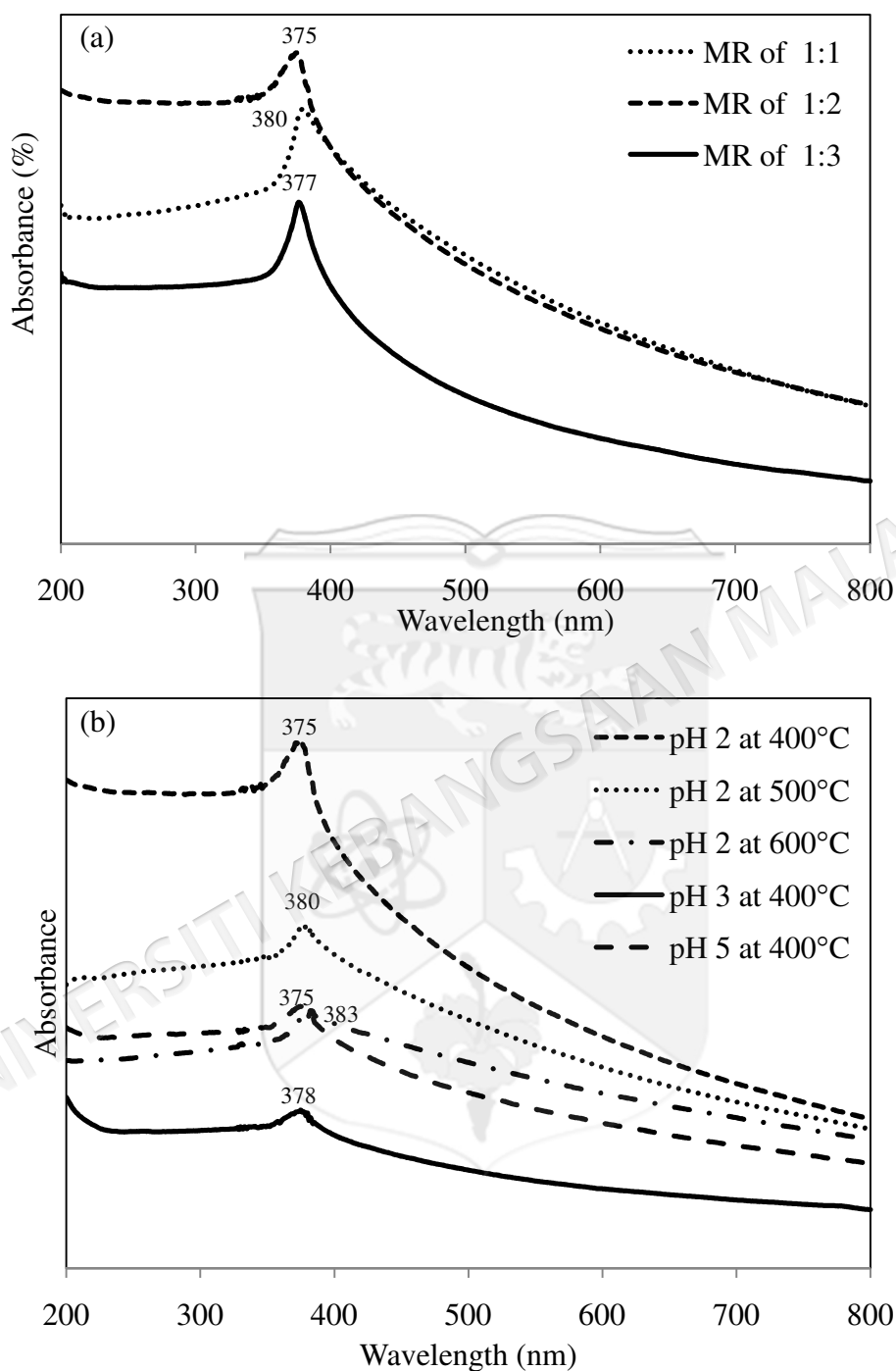


Figure 4.24 Absorption spectra of ZnO NP under different of (a) molar ratio, (b) pH and calcination temperatures.

4.6.2 Optical Properties of doped ZnO NP

ZnO NP is famous for many applications in industrial process due to their optical properties and morphology. To enhance of the optical properties, transition metals and some rare earth have been reported as a good doping for ZnO NP (Xu et al. 2009; Hassan et al. 2012). The optical properties of the ZnO and Fe^{3+} -doped ZnO NP with concentration of 0.25 to 1.0 wt.% under optimal conditions of molar ratio is 1:2, pH at 2.0 ± 0.2 and calcination temperature at 400°C were investigated by UV-vis measurement. Figure 4.25 shows all steps to estimate the band gap of ZnO and Fe^{3+} -doped ZnO NP using the diffuse reflectance and absorbance. The undoped ZnO NP spectrum shows an absorption onset at approximately 390 nm, which is in good agreement with the intrinsic energy band gap of ZnO at 3.198 eV. After doping, the absorption of the ZnO NP indicates the affecting of Fe^{3+} ions by changing the spectrum (Hassan et al. 2012).

The absorption spectra of Fe^{3+} -doped ZnO NP samples caused shifting to a longer wavelength which was also indicated by the change in catalyst color from white to reddish yellow. As concentrate of Fe^{3+} increase, a stronger absorption was recorded in the range of 400-600 nm (visible light region), which indicated a red shift in the band gap transition. The shift of absorption towards the red part of the spectra with Fe^{3+} doping was attributed to sp-d orbital exchange interactions between the band electrons in ZnO NP and the localized d electrons of the Fe^{3+} (Zhang et al., 2009).

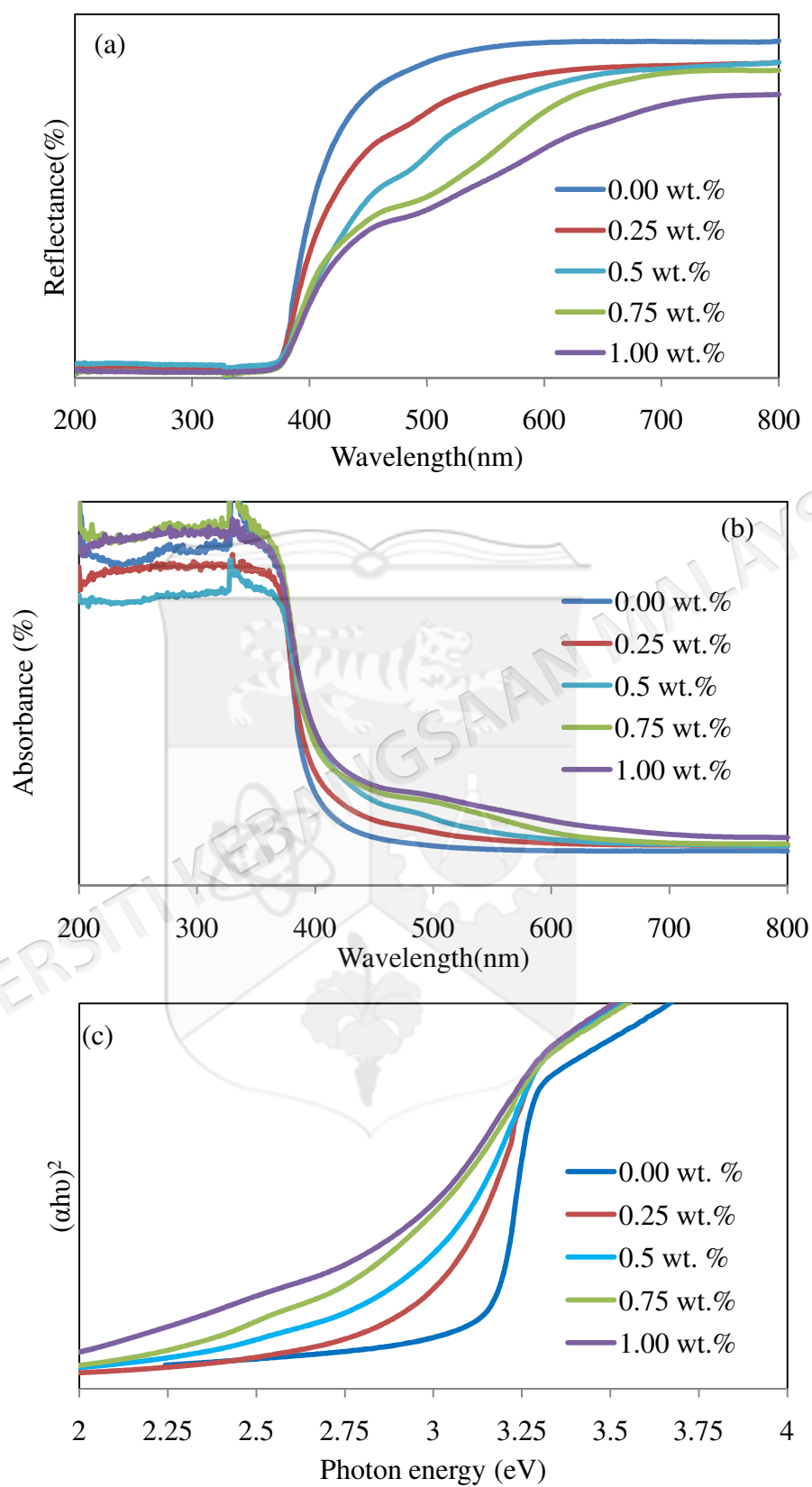


Figure 4.25 Optical properties of Fe³⁺-doped ZnO NP under optimal conditions (a) Diffuse reflectance, (b) Absorbance, (c) Band gap.

The Fe^{3+} ions in the valance band works as defects sits to reduce band gap was observed and shifting the absorbance to the visible light. The energy needs to transition from valance to conduction is lower energy than band gap of undoped ZnO. These results showed higher activity of Fe^{3+} -doping due to increases the absorbance in the visible light in which very useful parameter for photocatalyst application. The band gap of ZnO and Fe^{3+} -doped was found to decrease with an increasing Fe^{3+} doping concentration as presented in Figure 4.25 (c) and value given in Table 4.13.

The effects of Sm^{3+} ion doping on the optical absorption properties of ZnO NP were investigated using the diffuse reflectance and absorbance spectrum between 200 and 800 nm as shown in Figure 4.26 (a,b). A slight blue shift in the absorbance (i.e. an increase in the band gap) for the Sm^{3+} -doped ZnO samples was observed with an increasing concentration of the Sm^{3+} ions as reported earlier (Liu, et al. 2010). By plotting $(\alpha h\nu)^2$ as a function of the photon energy estimated for the band gaps of the various Sm^{3+} concentrations were used as shown in Figure 4.26 (c). Band gap energy results between 3.19 and 3.29 eV were obtained for concentration of 0.00 to 1.0 wt. % as given in Table 4.13. Increases in the band gap with the blue shift were attributed to the shift of Fermi levels close to the conduction band resulting in an increase in the carrier concentration, which blocks low energy transitions according to the Burstein-Moss effects (Nair et al. 2011). Increasing of absorption in UV region with Sm^{3+} concentrations increasing from 0.25 to 1.0 wt. % was observed as shown in Figure 4.26 (b). However, a slight improvement on absorption in visible (400 to 700 nm) which resulted no variations in band gap of Sm^{3+} -doped ZnO compare to ZnO NP pure.

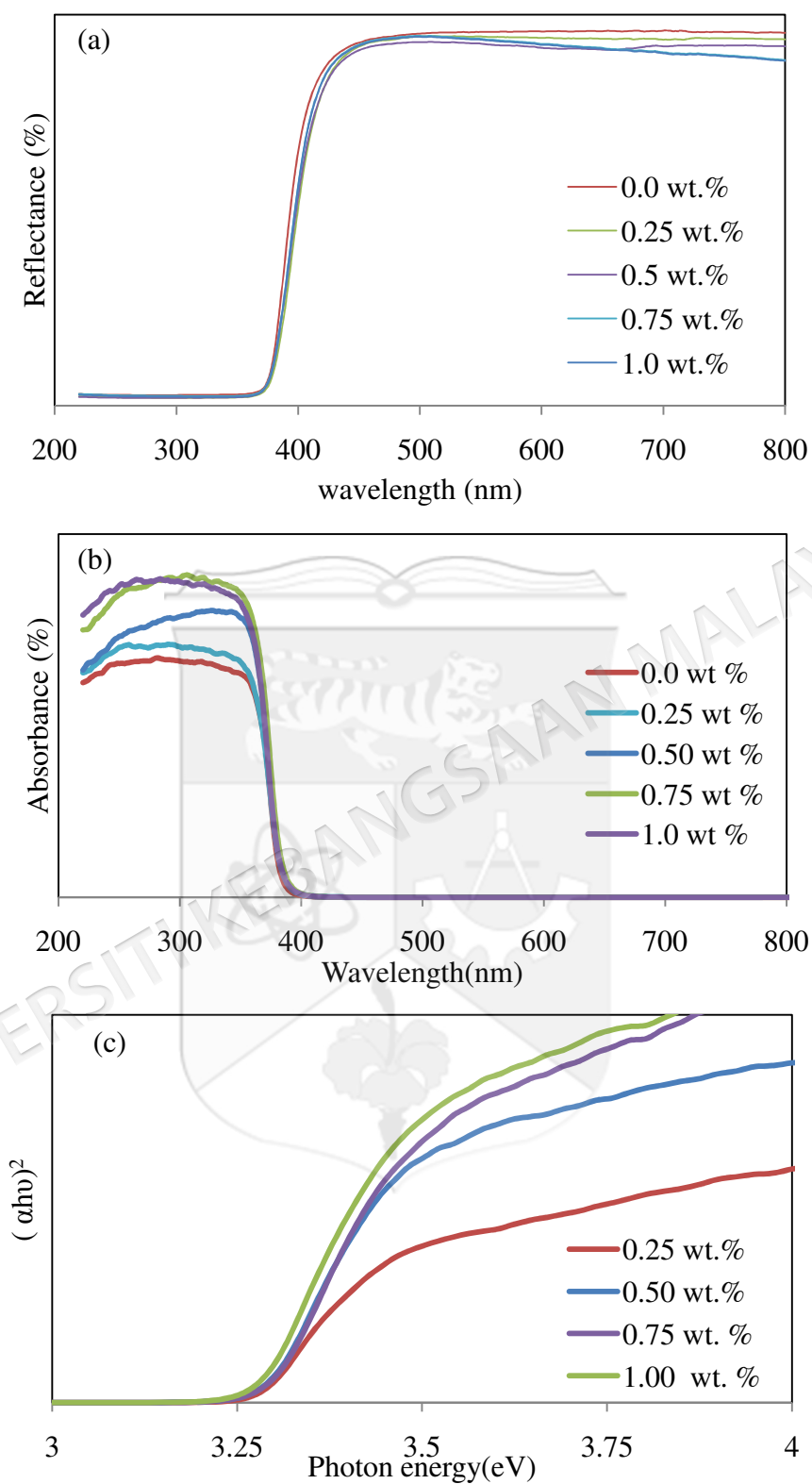


Figure 4.26 Optical properties of Sm^{3+} -doped ZnO NP under optimal conditions (a) Diffuse reflectance, (b) Absorbance, (c) Band gap.

Figure 4.27 (a,b) shows the diffuse reflectance and absorbance of Ti^{4+} -doped ZnO NP under range of 200- 800 nm with similar concentration of Fe^{3+} , Sm^{3+} between 0.00 to 1.00 wt. %. The reflectance indicates slight decrease with increased concentration under range 500 to 700 nm which attributed to absorption in the UV region according to optical band gap of the samples. As the particle size changed, the excitonic absorption shifted slightly which led to increases of band gap. The band gap was found from intercepts line as increasing slightly from 3.287 to 3.282 eV compared with undoped ZnO NP as given in Table 4.13.

The Ti^{4+} ions were substituted of Zn^{2+} in the ZnO matrix with slightly changing of lattice parameters as observed from the XRD spectrum. Therefore, Ti^{4+} gives two elections free after replacing Zn^{2+} which acted as donor atom and increasing the band gap due to increased the electrons concentration (carrier concentration) that leads to filling of lower states in the conduction band which was known Burstein-Moss effects. The increasing of band gap of Ti^{4+} -doped ZnO NP was observed shift from 3.40 to 3.60 eV for powder and from 3.29 to 3.86 for the thin films with concentration of Ti^{4+} from 0.00 to 4 wt. % (Lin et al. 2005). Generally, slight changes in the optical band gap of ZnO whit Sm^{3+} , Ti^{4+} doping, when lower concentration of dopants is used as indicated in this study. Furthermore, the results showed that the same mechanism for increasing the gap by same dopant but at higher concentration of Sm^{3+} , Ti^{4+} -doped ZnO NP was observed in this study and have been reported by a previous study (Liu et al. 2010).

Table 4.13 Band gap comparison of ZnO and doped ZnO NP using different ions and their concentrations

Concentration doping (wt. %)	Fe^{3+} doped	Sm^{3+} doped	Ti^{4+} doped
0.00	3.198	3.198	3.198
0.25	3.00	3.290	3.287
0.50	2.87	3.287	3.288
0.75	2.72	3.285	3.283
1.0	2.65	3.280	3.282

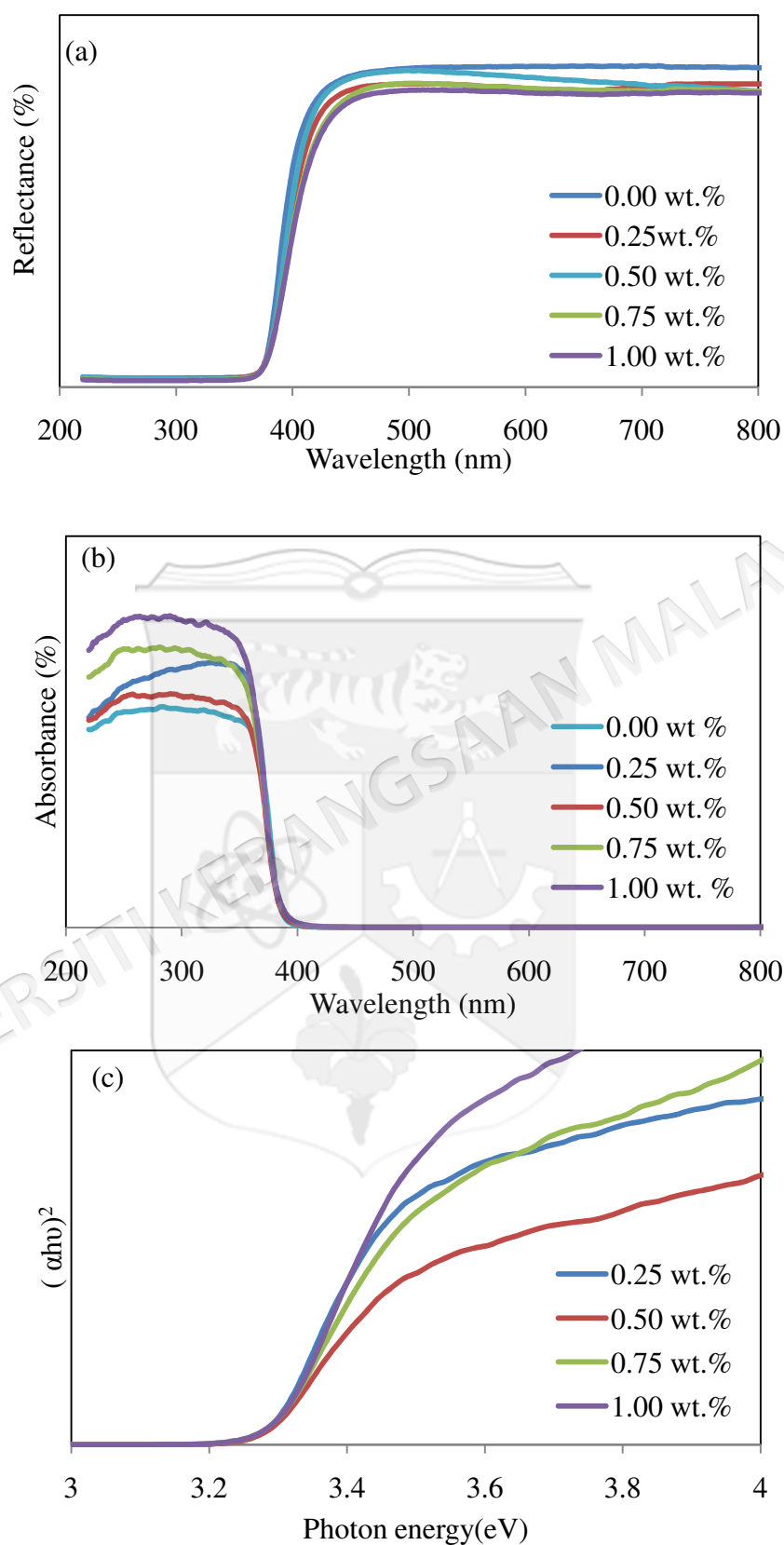


Figure 4.27 Optical properties of Ti^{4+} -doped ZnO NP under optimal conditions (a) Diffuse reflectance, (b) Absorbance, (c) Band gap.

4.7 SURFACE PROPERTIES ANALYSIS

The surface properties of semiconductor are very important to understand its behavior especially its surface phenomena for the environment applications. The surface properties shows more sensitive for the aqueous phase due to some specific adsorption of the material need to be photodecompose since these compounds are adsorbed on the photocatalyst surface. Surface property is considered as one factor for determine performance of the application and explain the activity within change of process parameters such as pH solution.

4.7.1 Zero- Point Charge of ZnO NP

The zero-point charge (pH_{zpc}) of undoped ZnO NP was investigated by zeta potential analysis under several of pH range between 4.0 to 11.0 ± 0.2 to determine the affects of process parameters. The pH_{zpc} of pure ZnO NP was found to be approximately 9.1 for all samples under different molar ratio, pH and selected calcinations temperature at 400, 500 and 600°C as demonstrated in Figure 4.28. The surface charge of undoped ZnO NP synthesized was found to be 9.1 ± 0.1 (with ± 5 mV of zeta potential values) which is in good agreement with earlier study (Lathasree et al. 2004). The surface is positively charged at a pH lower than 9 and it is negatively charged above pH 9. These results indicated that there was no effect of process parameters on the surface electrical charge of the ZnO NP because the ZnO NP is high purity with no impurities was detected. On the other hand, the sizes of particles were in the range between 20 to 45 ± 2 nm which that no changing in the pH_{zpc} was occurred as reported more than 100 nm in previous study of TiO_2 (Suttioponparnit et al. 2011). This suggestion was observed by results from XRD, TGA-DSC and EDX analysis. However, the experimental procedures of preparation method and properties plays main role to determine the final pH_{zpc} of nano-materials. The same size of TiO_2 particles produced different pH_{zpc} because different crystal phase was found (i.e anatase and rutile) (Suttioponparnit et al. 2011). The effect of temperature on pH_{zpc} of metal oxide at more than 250°C causes a decrease of pH_{zpc} value as reported by Muhammad et al. (2012). Therefore, it can be inferred that the adsorption of pollutants on to the surface of this catalyst within the application will be relatively minimized. The activity of photocatalyst nanoparticles for application have been influenced by the size of particle

and surface area in which decreasing size leads to surface sorption site increased (Tseng et al. 2012).

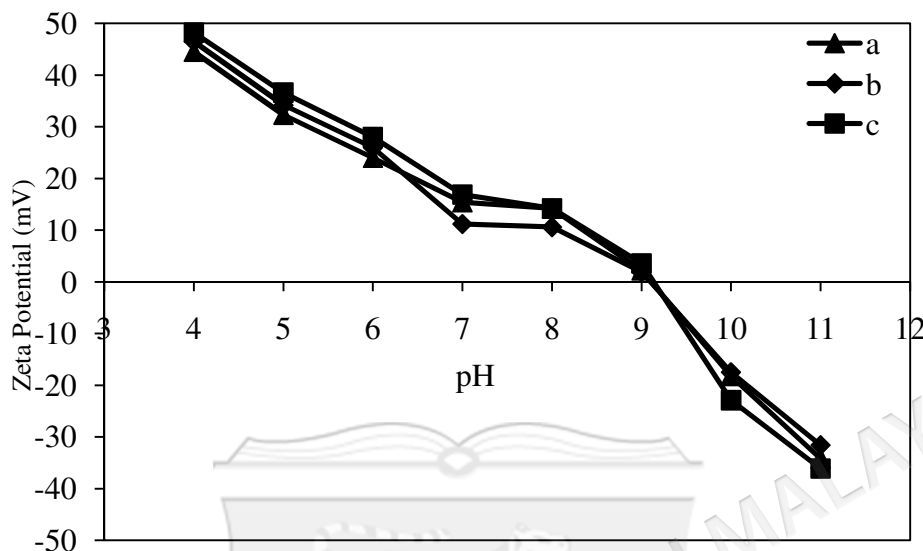


Figure 4.28 Zero point charge (pH_{zpc}) of undoped ZnO NP at different calcination temperatures (a) at 400°C, (b) 500°C, (c) 600°C.

4.7.2 Zero- Point Charge of Doped ZnO NP

The surface charge of doped ZnO NP using Fe^{3+} , Sm^{3+} and Ti^{4+} ions was determined under similar experimental procedures of undoped ZnO NP. Effects of Fe^{3+} , Sm^{3+} and Ti^{4+} ions on the pH_{zpc} of ZnO NP was evaluated with middle and higher concentrations. A pH_{zpc} value of doped ZnO NP indicated slight decrease from 9.1 to 8.85 for Fe^{3+} , Sm^{3+} and Ti^{4+} ions as given in Figure 4.29. The slight change in pH_{zpc} of all dopants may attributed to the small difference on the zeta potential as ± 5.0 mV due to the replacement of the dopant ions on ZnO matrix. However, the surface of all doped ZnO samples were positively charged in a solution with a pH of less than 9.0, and were negatively charged for a pH of more than 9.0. Furthermore, there is no effect on surface charge of doped ZnO using Fe^{3+} , Sm^{3+} and Ti^{4+} ions in the case of substitution in host of ZnO NP as reported earlier (Ahmed et al. 2012; Panigrahy et al. 2012).

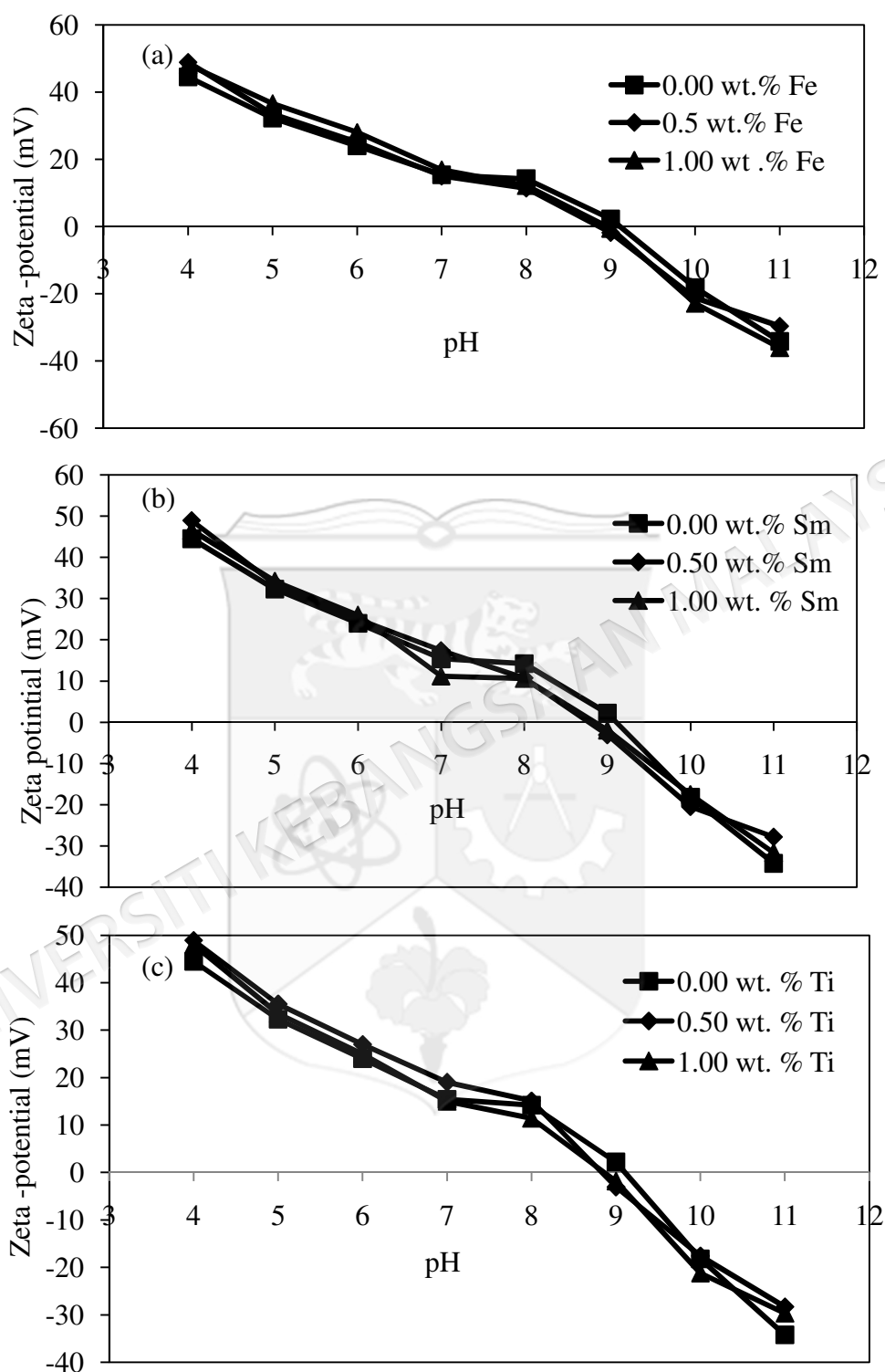


Figure 4.29 Zero point charge (pH_{zpc}) of doped ZnO NP with at different concentration of dopant Fe³⁺, (b) Sm³⁺, (c) Ti⁴⁺.

4.8 SURFACE AREA ANALYSIS

The surface area of the heterogeneous catalyst is one of important characteristics that affects on the quality and activity within process application. The Brunauer, Emmet and Teller (BET) has been reported as the most useful method to measure of the surface area based on the theoretical model for adsorption of monolayer by physical adsorption of gas molecules (Brunauer, 1938). The size, shape and porosity of the particle are the main factors that influence the on value of surface area. In the industrial catalyst the surface area and porosity are the factors that influence the physical interaction of catalyst with molecules in gases and liquids phase reaction. The surface area and porosity of ZnO and doped ZnO NP samples were measured using the BET method and discussed of affects all process parameters on final values of surface area.

4.8.1 Surface Area of ZnO NP

The effects of process parameters such as molar ratio, pH and calcination temperatures on ZnO NP surface area were evaluated using BET method with adsorption isotherms mechanism. Figure 4.30 shows the effect of the different parameters on the nitrogen adsorption-desorption isotherms and pore size of the ZnO NP powder. All samples of ZnO NP indicate that adsorption-desorption isotherms as V type according of IUPAC calcification for the sorption isotherms from which shows pore condensation and hysteresis (Sing et al. 1985). At higher relative pressure of P/P_0 of 0.8 to 0.99, the isotherm indicates the hysteresis loops as H1 based on the IUPAC calcification of hysteresis loops. This type of hysteresis loops shows the material is porous with the well defined cylindrical-like pore channel with uniform spheres of the particles (Sing et al. 1985). The average pore size distribution of all sample powder exhibits between 15 to 30 nm which confirmed that sample as mesopores (2-50 nm) type. The mesopores of sample follows the aggregation of almost uniform sphere particles of ZnO NP especially under optimum condition of preparation as reported earlier (Minghua et al. 2006).

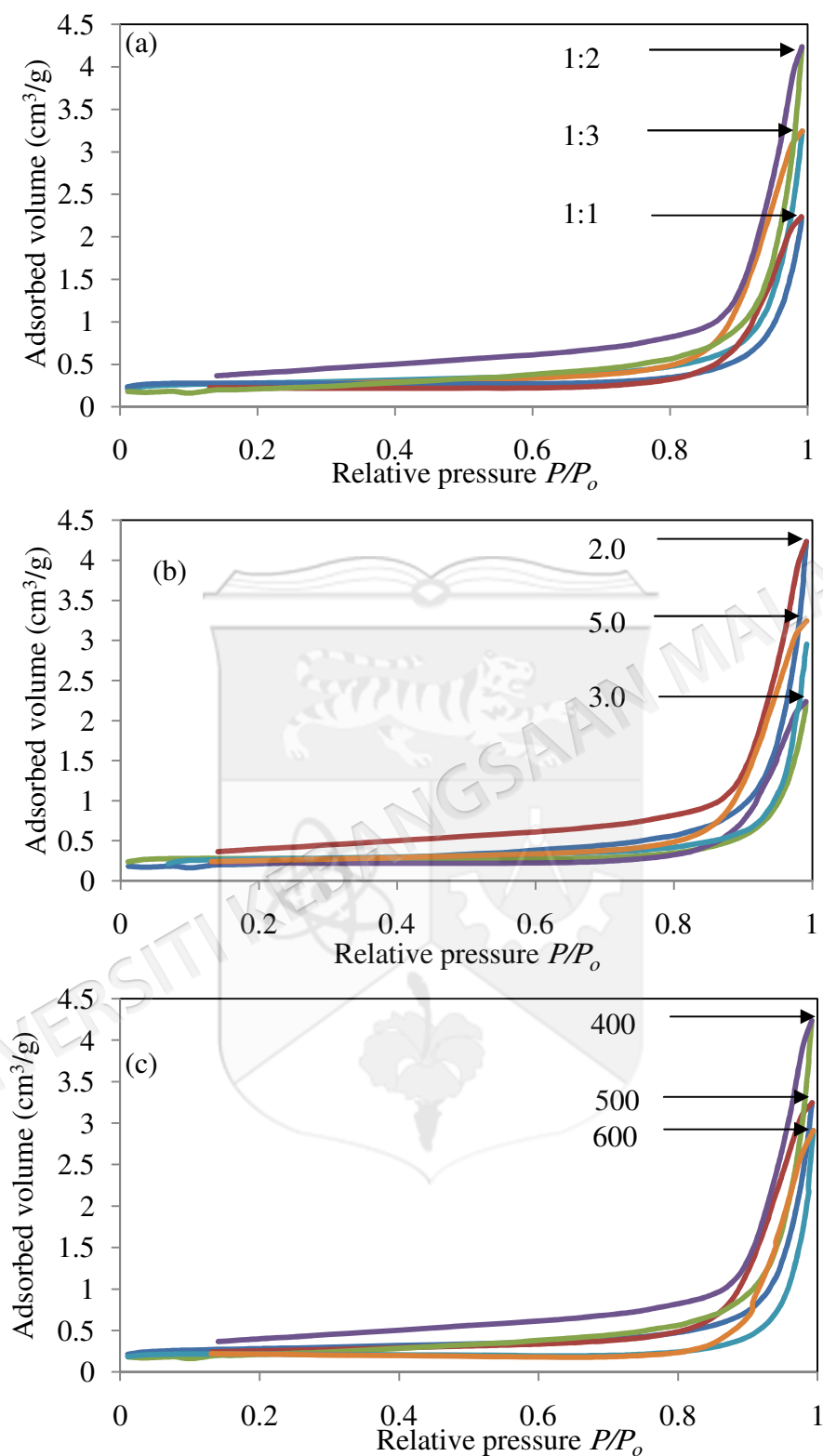


Figure 4.30 Nitrogen adsorption-desorption of ZnO NP prepared under different process parameters, (a) molar ratio, (b) pH, (c) calcination temperatures.

The surface area, pore volume and average pore size of ZnO NP prepared under different conditions were summarized in Table 4.14. Lower value of surface area of molar 1:1 and 1:3 compare to 1:2 was observed which due to 1:1 has significant agglomeration between the particle and 1:3 also bigger particle than 1:2 was obtained as confirmed by the FESEM and TEM results (section 4.5.1). Same sequence of the molar ratio affects was observed which attributed to varying of the particle size led to change in surface area. However, the agglomeration and porosity of the particles has affect on surface area values as reported earlier (Minghua et al. 2006). Effects of pH on morphology and size of ZnO NP indicates main factor to determine the final surface area. A pH of 3.0 shows a bigger size was produced as confirmed by the XRD, FESEM and TEM (section 4.5.1) which led to lower area compared to optimum pH of 2.0. A higher agglomeration of ZnO NP shows at pH 5.0 with slightly smaller size of particle compared with pH 3.0 was obtained. Therefore the surface area was remained lower than optimum pH with slight increase compared to pH 3.0.

Table 4.14 Surface properties of ZnO NP under several condition of preparation

Molar ratio (Z_{Ac}: O_{xAc})	pH	Calcination Temperature (°C)	Crystal size by XRD (nm) ±2	Surface area (m²/g)	Pore volume (cm³/g)	Average pore (nm)
1:1	2.0±0.2	400	30	16.8	0.1480	19.3889
1:2	2.0±0.2	400	18	26.2	0.1123	25.2807
1:3	2.0±0.2	400	35	19.2	0.1648	17.6724
1:2	3.0±0.2	400	32	18.2	0.1715	16.1733
1:2	5.0±0.2	400	28	20.0	0.1123	25.2807
1:2	2.0±0.2	500	27	16.0	0.1434	18.7654
1:2	2.0±0.2	600	35	13.8	0.0909	29.7763

The more significant affecting of the calcination temperature was observed which increases of particle size lead to decreasing of surface area as liner relationship.

However, the the pore size increased slightly with higher temperature indicating that bigger particle was grew (Seetawan et al. 2011). This result also was discussed and reported on the result obtained from XRD, FESEM and TEM data (section 4.5.1). Generally, it can be seen the nitrogen adsorption-desorption isotherms graphs were affected by different conditions of molar ratio, pH and calcination temperature. The relative of pressure and hysteresis loops in range of 0.8 to 0.99 increases with the surface area increasing indicating that the porous are mesopores (type V) (Minghua, et al. 2006).

4.8.2 Surface Area of Doped ZnO NP

Effects of the doping process using Fe^{3+} , Sm^{3+} and Ti^{4+} ions with concentration between 0.00 to 1.0 wt.% on surface area of ZnO NP was investigated. Figure 4.31 shows the nitrogen adsorption-desorption isotherms graph of all doped ZnO NP samples with calcined at 400°C. All doped ZnO NP samples exhibits the V type of adsorption-desorption isotherms based on the IUPAC calcification for the sorption isotherms. Additionally, the hysteresis loops as H1 based on the IUPAC calcification of hysteresis loops was reported in the range of 0.8 to 0.99 (Sing et al. 1985). All surface properties such as surface area, pore volume and average pore size of doped ZnO NP samples were given in Table 4.15 and compared with ZnO undoped NP. With increasing concentrations of all dopants, the volume of adsorbed gas increased with hysteresis loops became boarded under range of relative pressure of 0.8 to 0.99.

These results attributed to the increasing of the surface area with the concentration increased for all dopants compared with undoped sample which have been reported earlier (Minghua et al. 2006). From Table 4.15, at low concentration (0.25 wt. %) of all dopants showed the areas almost close to $26.8 \pm 0.2 \text{ m}^2/\text{g}$ compared to undoped ZnO of $26.2 \text{ m}^2/\text{g}$. This result confirmed that doping enhances of surface area of ZnO NP even at low concentration (Pathak & Purohit 2013). However, the concentration of Fe^{3+} , Sm^{3+} and Ti^{4+} ions at 0.5 wt. % and above, significant increase surface area was observed.

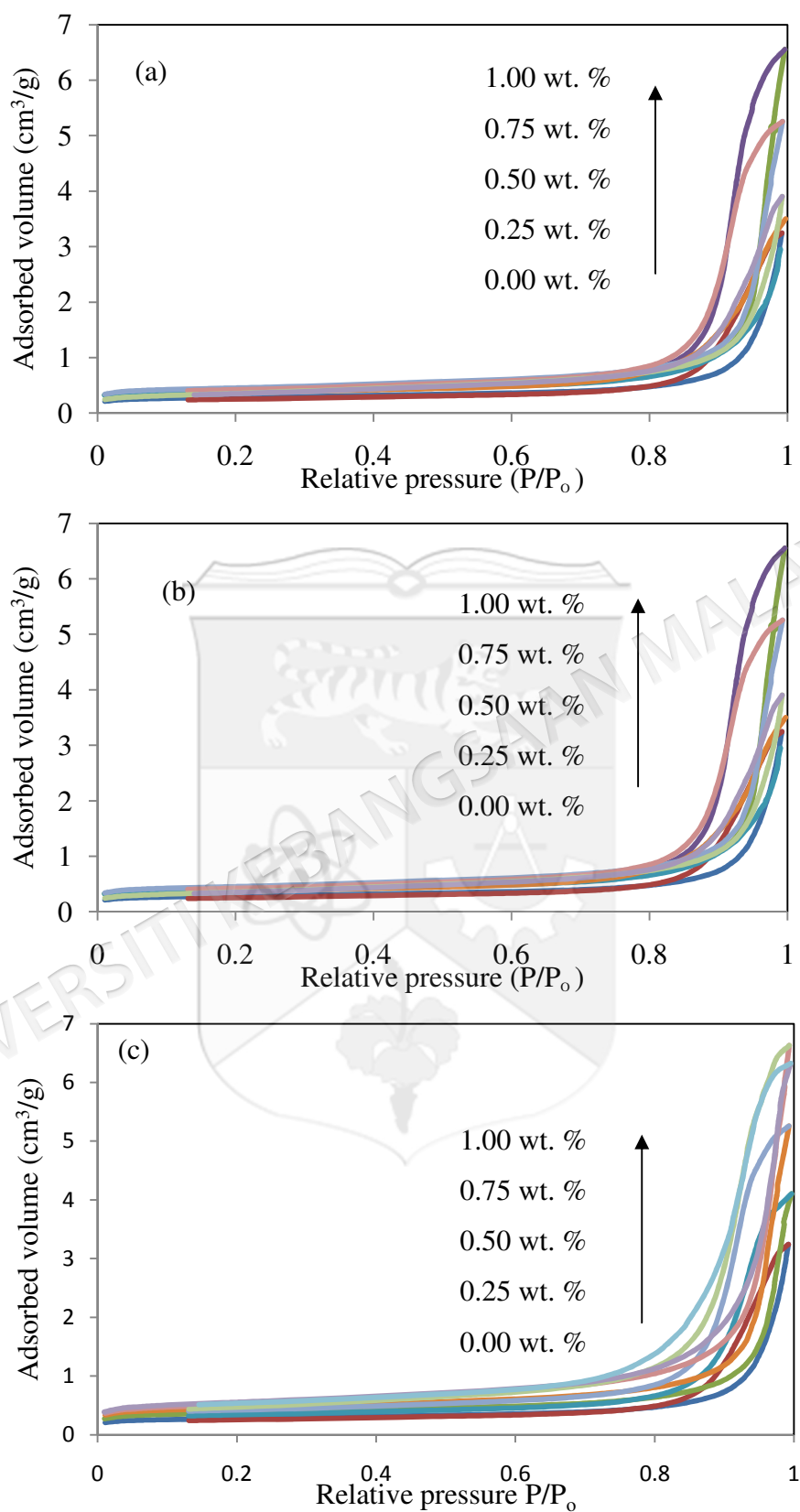


Figure 4.31 Nitrogen adsorption-desorption of doped ZnO NP with (a) Fe^{3+} , (b) Sm^{3+} , (c) Ti^{4+} -doped ZnO.

The surface area of doped ZnO by $\text{Fe}^{3+} \leq \text{Sm}^{3+} < \text{Ti}^{4+}$ was found for concentration more than 0.25 wt. %. The highest surface area was obtained when Ti^{4+} was used due smaller size of particle which confirmed by XRD and TEM analysis (section 4.5.2). Moreover, smaller pore size of Ti^{4+} doped ZnO samples then compared to Fe^{3+} and Sm^{3+} as reported in Table 4.15. Generally, with increasing doping concentration, the average pore size decreases, which could be attributed to the aggregation of smaller crystallites (Paola et al. 2011).

Table 4.15 Surface properties of doped ZnO NP with different ions

Doping by Wt. %	Crystal size by XRD (nm) ± 2	Surface area (m^2/g)	Pore volume (cm^3/g)	Average pore size (nm)
0.0	18	26.2	0.1123	25.20
0.25	^a 16.10	^a 26.8	^a 0.1663	^a 24.19
	^b 15.80	^b 26.6	^b 0.1360	^b 24.40
	^c 15.56	^c 26.9	^c 0.1420	^c 24.39
0.5	^a 15.00	^a 27.8	^a 0.1649	^a 21.51
	^b 13.60	^b 28.3	^b 0.1718	^b 23.60
	^c 13.38	^c 32.7	^c 0.1765	^c 21.50
0.75	^a 13.20	^a 30.1	^a 0.1761	^a 22.77
	^b 13.01	^b 31.3	^b 0.1766	^b 21.90
	^c 12.20	^c 38.6	^c 0.2301	^c 21.59
1.0	^a 11.82	^a 31.2	^a 0.2274	^a 24.40
	^b 12.70	^b 32.7	^b 0.2273	^b 21.50
	^c 11.50	^c 40.9	^c 0.2198	^c 19.28

^a Fe^{3+} doped ZnO, ^b Sm^{3+} doped ZnO, ^c Ti^{4+} doped ZnO

CHAPTER V

APPLICATION OF ZnO NP IN PHOTOCATALYTIC REACTION

5.1 INTRODUCTION

The optimization of the photocatalytic process using the design of experiment (DOE) based on the RSM has been reported as being a more efficient tool for studying the effects of all parameters. However, the RSM has also been used to estimate the value of optimum parameter levels to create a good fit for the final model (Korbahti et al. 2008). The condition of the experimental design for the photocatalytic degradation process is considered to be the critical point for determining the optimum conditions for a catalytic reaction. The experimental optimization with a theoretical concept based on the RSM helps to develop an overall process for the future (Sakkas et al. 2010).

5.1.1 Factors Screening for Photocatalytic Experiments

In this study, the first step towards the creation of a photocatalytic process model is the screening, which determines the most significant parameters (factors) which affect the final response (output). The photocatalytic degradation efficiency (DE %) of chlorophenols was selected as the response of the process. However, the parameters affecting the response (DE %) were chosen with their levels and are given in Table 5.1. The selection of the factors was based on the preliminary results of experiments and some previous studies which had indicated the type of factors and their levels (Safaei et al. 2010).

Table 5.1 Photocatalytic degradation parameters and their levels

Independent variables	Factor	levels	
	X_i	-1	+1
PH	X_1	4	8
ZnO loading (g/l)	X_2	1	3
Calcination Temperature ($^{\circ}\text{C}$)	X_3	400	600
Solar intensity (W/m^2)	X_4	10	20
Initial concentration(mg/l)	X_5	50	150

The two-level factorial design was applied as a good and appropriate design for reducing the parameters by removing the insignificant ones and recognizing those that have a significant effect on the final response (Box et al. 2005). The Design-Expert version 6.0.6 (Stat-Ease Inc. MN, USA) software was applied to a two-level factorial design with an all data analysis. 16 runs with lower and higher levels were produced by the two-level factorial design for five selected factors and were summarized with the results of the response in Table 5.2. Each experiment was prepared under certain conditions of the run which started with a 100 ml solution of 2-CP (as an example of chlorophenols) at different concentrations of between 50 to 150 mg/l. The batch slurry reactor (cylinder) was used with 60 minutes of irradiation time for all the experimental runs. After adjusting the pH of the solution for 4 or 8 values using HCl or NaOH, a certain loading of ZnO NP for 1 or 3 g/l was added and stirred for 30 minutes under dark conditions. Then the samples were exposed to direct solar radiation under lower (cloudy day) or higher (sunny day) intensity between 11.00 to 12.00 a.m. according to the run condition of the screening.

To determine the degradation efficiency, after 60 minutes a particular sample was collected and centrifuged. It was then filtered by passing it through $0.45\ \mu\text{m}$ and then analysed. The monitoring of the final concentration was calculated based on the 2-CP standard using the HPLC and UV-vis spectrophotometer. The most significant factors for the photodegradation efficiency were tested after experiments by the ANOVA analysis as shown in Table 5.3. The model of the screening process indicated that the P-value (< 0.0001) was very much lower than 0.05. Additionally, the most

significant factors were the pH of the solution (X_1), the calcination temperature (X_3) and the solar intensity (X_4) with a P-value of < 0.050 .

Table 5.2 Response results of screening design using two-level factorial design

Std	Run No.	X_1	X_2	X_3	X_4	X_5	DE% (Act.)	DE% (Per.)
1	4	4	1	400	10	150	38.13	39.401
2	7	8	1	400	10	50	34.558	35.912
3	1	4	3	400	10	50	36.94	43.491
4	6	8	3	400	10	150	36.13	34.492
5	14	4	1	600	10	50	29.52	29.122
6	8	8	1	600	10	150	22.68	20.123
7	11	4	3	600	10	150	30.82	27.702
8	3	8	3	600	10	50	25.68	24.213
9	2	4	1	400	20	50	60.558	56.141
10	13	8	1	400	20	150	46.33	47.141
11	9	4	3	400	20	150	53.166	54.721
12	12	8	3	400	20	50	56.72	51.231
13	10	4	1	600	20	150	41.04	40.352
14	5	8	1	600	20	50	32.24	36.862
15	15	4	3	600	20	50	45.2	44.442
16	16	8	3	600	20	150	31.08	35.442

The model regression resulted in higher coefficients of R^2 and R^2_{adj} , with values of 0.9110 and 0.8664, respectively being obtained. These results showed that R^2 and R^2_{adj} were in good correlation and were a good fit of the experimental results to the predicted results as shown in Table 5.3.

Table 5.3 ANOVA results for screening using two-level factorial design

Source	Sum of squares	Degree of freedom	Mean square	F-value	P-value
Model	1655.27	5	331.05	20.46	$< 0.0001^*$
X_1	155.98	1	155.98	9.64	0.0112 *
X_2	7.13	1	7.13	0.44	0.5218**
X_3	679.54	1	679.54	42.00	$< 0.0001^*$
X_4	782.26	1	782.26	48.35	$< 0.0001^*$
X_5	30.36	1	30.36	1.88	0.2007**
Residual	161.78	10	16.18		

*Significant at $< 0.05\%$ level; ** Not significant, $R^2 = 0.9110$, $R^2_{adj} = 0.8664$, Std. Dev.= 4.02, Mean=38.80, C.V= 10.37, Adeq Precision=14.623.

The first order of model equation was found for all selected parameters (factors) of screening process as follows:

$$\text{Degradation Efficiency (DE\%)} = 61.19450 - 1.56112 X_1 + 0.66750X_2 - 0.065170 X_3 + 1.39845 X_4 - 0.027550X_5 \quad (4.5)$$

Some characteristics of the model screening such as the normality, residual, outlier and predicted results are summarized in Figure 5.1.

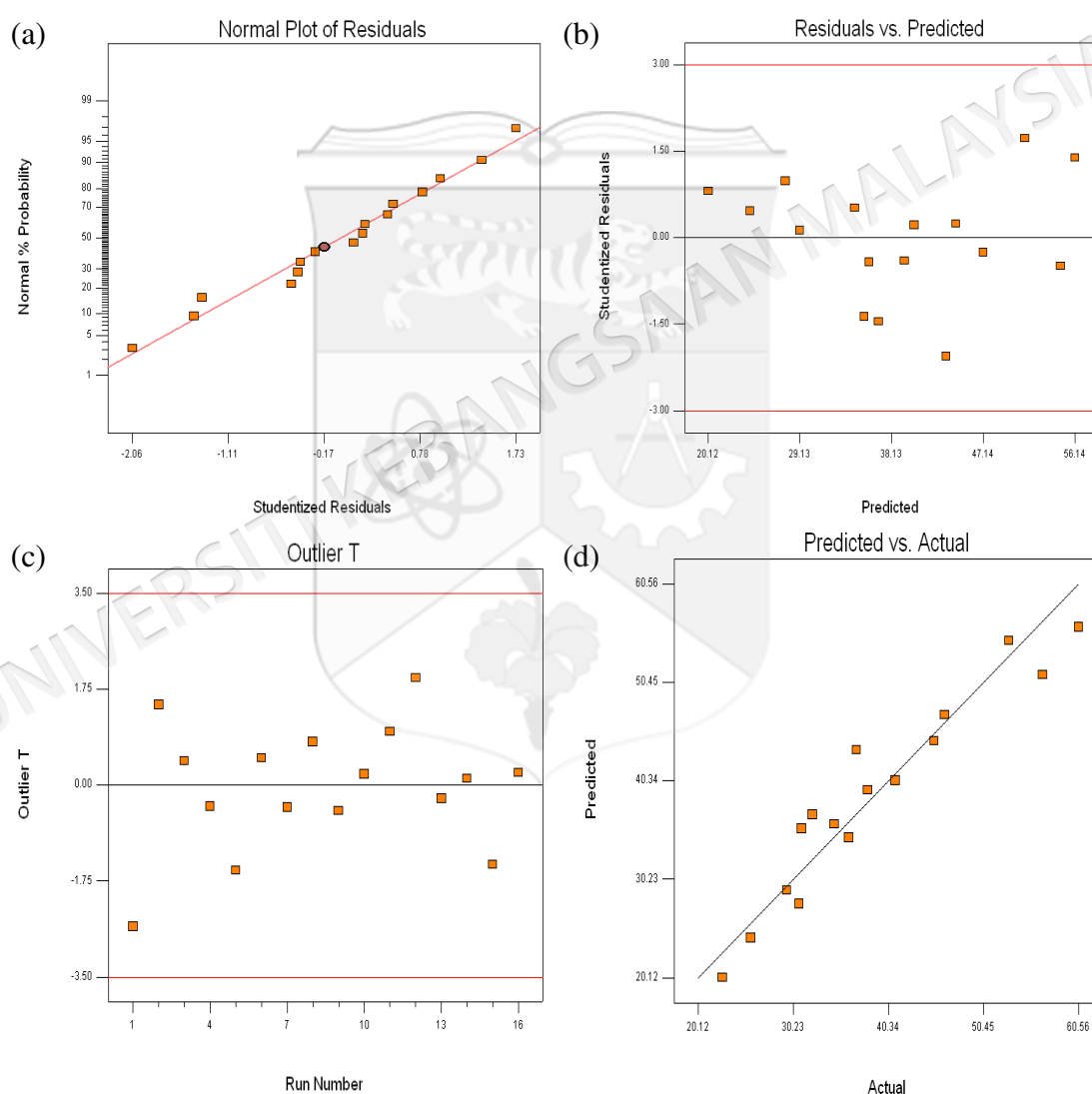


Figure 5.1 Some characteristics of the model screening, (a) Normality, (b) Residual. (c) Outlier test, (d) predicated and actual results.

The normality versus the studentized residual plots is shown as being very close to the line, which indicates good assumptions by the ANOVA results without any problem with the model. However, a random scattering experiment investigated that response, and the original observation of variance showed that there was no problem between the response and the factors. The outlier plots of all the experimental runs exhibited a good distribution and there was no occurrence of any problems. The actual value of the DE % against what was predicted by all the experiments showed that a higher R^2 and R^2_{adj} were produced with good accuracy in the final model of the DE % as the response.

The effects of each factor and the overall effects were arranged based on the pareto plot from the maximum to the minimum as shown in Figure 5.2 (a). It was observed that the first three factors, that is, the solar intensity, calcination temperature, and pH of the solution had the greatest effect compared to loading and concentration. Furthermore, the effect of the factors on the photodegradation efficiency was estimated in Figure 5.2 (b), which showing that solar intensity had a more positive effect, while loading had only a slight effect, on increasing the efficiency. On the other hand, a decrease in efficiency due to the negative effects of the pH, calcination temperature, and concentration of the pollutant was reported by other experimental studies (Khayyat et al. 2012).

The efficiency of photocatalytic degradation has been reported to be negatively affected by the pH of a solution when the pH value is higher or lower than the optimal value within the process (Pardeshi & Patil 2008). The pH affects the adsorption of chlorophenols on the surface of ZnO, thus significantly affecting the efficiency of the photocatalytic degradation since the photocatalytic reaction occurs on the surface of the ZnO. Moreover, the rate of reaction increases with loading which shows a positive effect on the degradation. The explanation for this result may be that the active sites are more available to degrade more molecules on the surface of the ZnO NP (Behnajady et al. 2006). It was observed that the calcination temperature had a negative effect on the degradation of chlorophenols by ZnO NP.

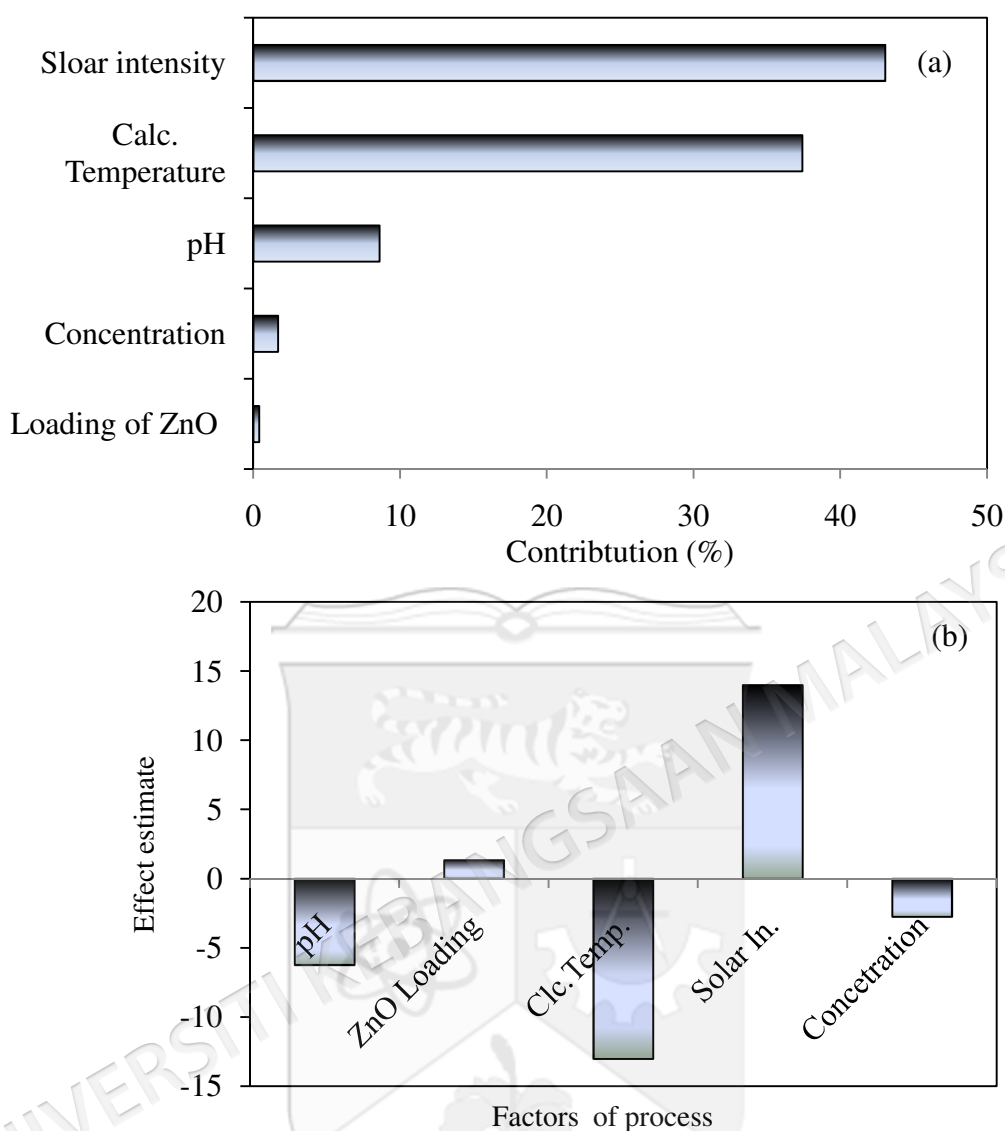


Figure 5.2 Pareto plot for (a) Effect of factors (b) Estimate effects of factors on degradation efficiency.

The bigger particle size and pore size of the ZnO NP have been reported as being the main reason for the decrease in surface area within the calcination process (Seetawan et al. 2011). The degradation efficiency decreased when the calcination temperature was applied at 400, 500, and 600°C due to the rapid decrease in surface area which was attributed to lower adsorption of chlorophenol molecules on the surface of the ZnO. At the same time, the solar intensity was found to have a more positive effect on sunny days compared to cloudy days. This result is attributed to the higher energy absorbed by the ZnO NP leading to the generation of more species of e^- , h^+ , $OH^\bullet$ and $O_2^- \bullet$ to enhance the reaction rate (Herrmann 2005). The initial

concentration of chlorophenols as one of the parameters shows that it has a negative effect on the photocatalytic degradation of chlorophenols. Increasing the chlorophenol concentration leads to greater absorption of molecules on the surface of the catalyst, which is attributed to the decrease in the reaction rate of the degradation process (Fenoll et al. 2012).

5.1.2 Optimization of Photocatalytic Process Using RSM

To complete the optimization process, the most significant factors were selected after screening for the pH of the solution, the solar intensity, and the calcination temperature. Moreover, it has been reported that the highest surface area and optical properties of the ZnO NP help to test the photocatalytic degradation activity of the pollutant under direct solar irradiation (Pardeshi & Patil 2008). For greater photocatalytic efficiency, the statistical design of experiment based on the RSM was applied. The RSM-based D-optimal design was chosen to continue this study from the synthesis to its application, where this design was expected to produce a higher accuracy for the final response as reported in the literature review. The most significant factors with their levels and codes for the optimization of the photocatalytic process are given in Table 5.4.

Table 5.4 Parameters and their levels for optimization of photocatalytic process

Independent variables	Factor	levels		
	X_i	-1	0	+1
PH	X_1	4	6	8
Calcination Temperature ($^{\circ}\text{C}$)	X_2	400	500	600
Solar intensity (W/m^2)	X_3	10	15	20

The same experimental procedures for the screening process were applied for the optimization, with fixed ZnO NP loading at 2 g/l and concentration of 2-chlorophenol at 50 mg/l. These values were selected according to the results of experiments where the optimum conditions for the highest efficiency of degradation were applied. The results of the degradation efficiency (DE %) and the removal of dissolved oxygen (COD %) tested under different conditions of these factors were

recorded and are presented in Table 5.5 together with a comparison to the predicted values (with error < 5%). The degradation efficiency and COD % were found to be almost in agreement with the predicted values from the model. The results of the experiments based on the D-optimal design were analysed by ANOVA and the final regression equation for the responses was created for the model with factor codes as given in Equations (5.1) and (5.2):

$$\begin{aligned} \text{DE\%} = & -200.80058 + 15.30287 X_1 + 0.47468 X_2 + 13.07128 X_3 - 1.16098 X_1^2 - \\ & 4.40184\text{E-}004X_2^2 - 0.16438X_3^2 - 9.01719\text{E-}004X_{12} - 0.030043X_{13} - \\ & 8.40433\text{E-}003X_{23} \end{aligned} \quad (5.1)$$

$$\begin{aligned} \text{COD \%} = & -222.58805 + 19.42393 X_1 + 0.45193X_2 + 14.71225 X_3 - 1.38626 X_1^2 - \\ & 3.77796\text{E-}004X_2^2 - 0.17419X_3^2 - 2.08309\text{E-}003X_{12} - 0.080139X_{13} - \\ & 0.010618X_{23}. \end{aligned} \quad (5.2)$$

Table 5.5 Actual and predicted results of optimization based on D-optimal design with DE% and COD % responses.

Std	Run No.	X ₁	X ₂	X ₃	DE% (Act.)	DE% (Per.)	COD % (Act.)	COD % (Per.)
1	14	4	400	10	37.80	39.29	32.72	33.94
2	11	8	400	20	88.27	87.51	84.84	84.54
3	15	4	400	20	84.53	85.87	82.27	83.13
4	18	8	600	20	59.83	59.35	53.42	53.56
5	7	6	600	10	30.80	34.36	29.69	32.88
6	9	6	400	15	73.05	72.45	70.30	69.94
7	6	8	500	15	58.98	63.45	55.15	59.57
8	13	6	500	20	80.28	81.83	76.24	78.08
9	5	8	400	10	38.53	42.13	35.75	38.56
10	1	4	600	15	47.01	47.65	43.69	44.19
11	17	5	500	15	61.05	55.03	57.03	51.49
12	10	4	600	10	28.71	28.66	25.72	25.86
13	16	8	600	10	33.46	30.77	31.75	28.81
14	12	4	600	20	58.93	58.43	54.18	53.82
15	4	8	600	20	59.83	59.35	54.57	53.56
16	3	4	400	20	86.53	85.87	83.69	83.13
17	8	8	400	10	45.77	42.13	41.21	38.56
18	2	8	400	20	88.57	87.51	86.51	84.54

Some characteristics and diagnostic plots of the optimization process based on the D-optimal design are presented in Figure 5.3. All the points of the experiments

appeared near the line confirming that there was no problem with the model with good assumptions by the ANOVA results. These results were confirmed by the normal probability versus the studentized residual plots as shown in Figure 5.3 (a). The random scattering of the experimental points compared to the funnel-shaped pattern that was obtained indicates that the DE % response had an original observation of variance with no problem between the response and the factors, as given in Figure 5.3 (b) (Box et al. 2005).

Figure 5.3 (c) exhibits the main characteristic to continue the model analysis is outlier in which indicated that good distribution of experiment points and none them out of the range. The actual value of the DE % with the predicted value of the model was evaluated by the value of R^2 and R^2_{adj} as plotted in Figure 5.3 (d). Generally, these coefficients have been influenced by the insignificant factor that resulted from the ANOVA analysis when the range of the factors and the limited number of runs play a main role for increases or decreases in the R^2 and R^2_{adj} values. The R^2 and R^2_{adj} values, which were 0.9847 and 0.9676, respectively show that a good model was created to explain the optimization conditions for the degradation process. The studentized residuals for the experimental runs are shown in Figure 5.3 (e), which indicates how many standard deviations occurred for the actual result value that deviated from the predicted value. The value of the studentized residuals occurred almost at intervals between -3.5 to +3.5, and the observed response value was not respected for any value that was more or less than this value (Korbahti et al. 2008). This model has values for the studentized residuals which are lower than ± 3.5 , which give a good fitting of the model to the response surface.

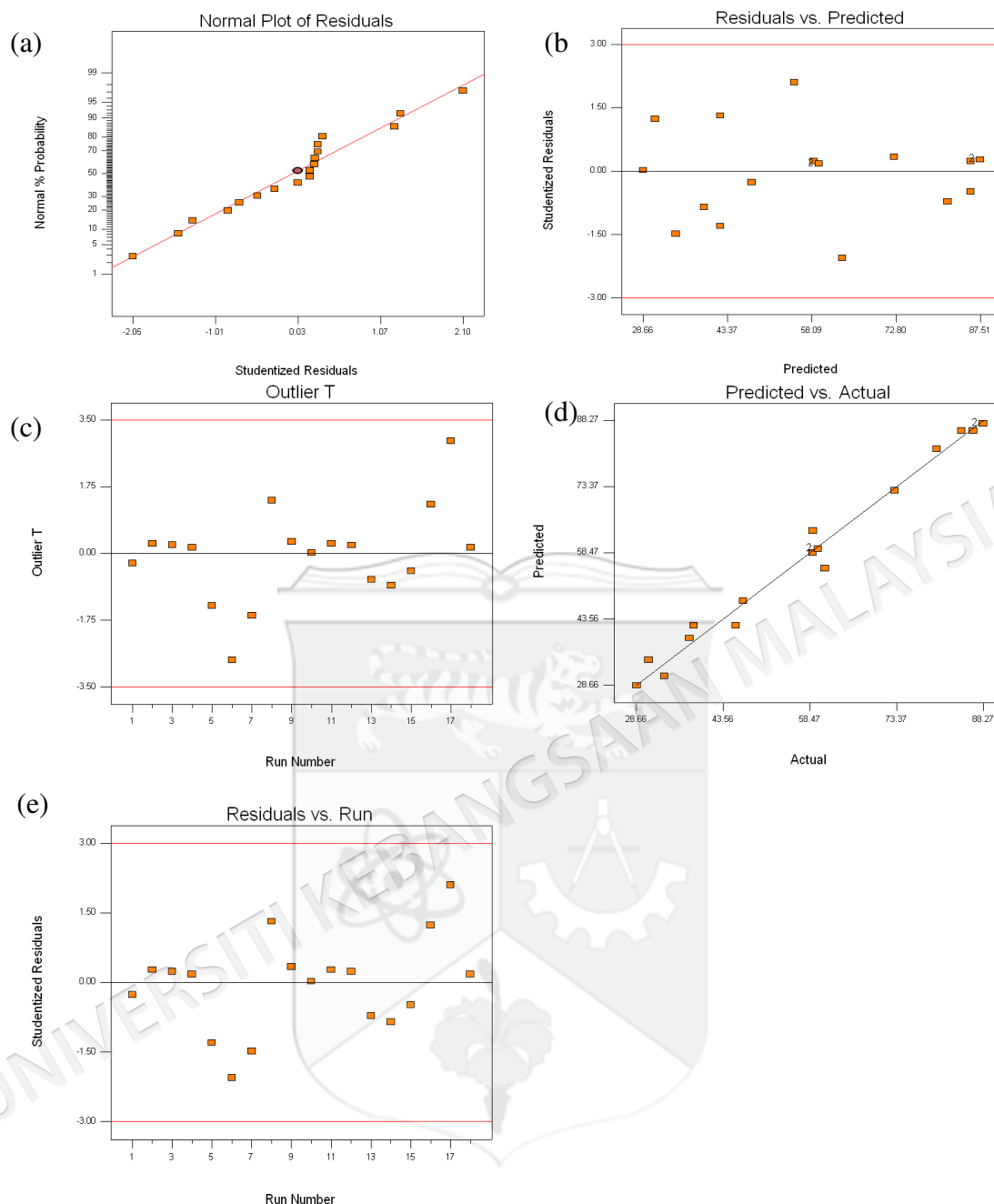


Figure 5.3 Diagnostic plots of the degradation efficiency for optimization process

The ANOVA results of the DE% and COD models are summarized in Table 5.6 and Table 5.7 respectively, with the significance of all the factors being according to the p-value. The p-value for each factor that is less than 0.05 (< 0.050) is significant, otherwise any p-value that is more than 0.05 (> 0.050) is not a significant factor for the model. The more significant factors were the calcination temperature (X_2) and solar intensity (X_3) with the linear effects on the model. However, the pH of the solution (X_1) had no effect on the final response as the p-value was greater than

0.05. The value of the adequate precision was 21.116 and 22.519, for DE% and COD respectively, which greater than the desirability value of 4 and indicates a single adequacy (Korbahti et al. 2009). Moreover, the lack of fit was found to be 2.96 and 4.91 (F-value), which is also insignificant relative to the pure error.

Table 5.6 Analysis of variance (ANOVA) for the DE% of 2-CP

Source	Sum of squares	Degree of freedom	Mean square	F-value	P-value
Model	7218.73	9	802.08	57.37	<0.0001*
X ₁	11.30	1	11.30	0.81	0.3948 **
X ₂	1336.19	1	1336.19	95.57	< 0.0001*
X ₃	4523.99	1	4523.99	323.58	< 0.0001*
X ₂₁	45.40	1	45.40	3.25	0.1092 **
X ₂₂	33.05	1	33.05	2.36	0.1627**
X ₂₃	35.55	1	35.55	2.54	0.1495**
X ₁₂	0.40	1	0.40	0.028	0.8706**
X ₁₃	1.01	1	1.01	0.072	0.7951**
X ₂₃	214.67	1	214.67	15.35	0.0044*
Residual	111.85	8	13.98		
Lack of fit	83.59	4	20.90	2.96	0.1593**
Pure error	28.26	4	7.07		
Total	7330.58	17			

*Significant at < 0.05% level; ** Not significant, $R^2 = 0.9847$, $R^2_{adj} = 0.9676$, Std. Dev. = 3.74, Mean=58.98, C.V= 6.34, Adeq Precision=21.116.

Table 5.7 Analysis of variance (ANOVA) for the COD % of 2-CP

Source	Sum of squares	Degree of freedom	Mean square	F-value	P-value
Model	7242.73	9	804.75	65.85	<0.0001*
X ₁	15.24	1	15.24	1.25	0.2965 **
X ₂	1324.36	1	1324.36	110.83	< 0.0001*
X ₃	4378.60	1	4378.60	358.30	< 0.0001*
X ₂₁	64.72	1	64.72	5.30	0.0504 *
X ₂₂	24.35	1	24.35	1.99	0.1958**
X ₂₃	39.92	1	39.92	3.27	0.1083**
X ₁₂	2.11	1	2.11	0.17	0.6887**
X ₁₃	7.17	1	7.17	0.59	0.4656**
X ₂₃	342.64	1	342.64	28.04	0.0007*
Residual	97.76	8	12.22		
Lack of fit	81.23	4	20.31	4.91	0.0761**
Pure error	16.23	4	4.13		
Total	7340.50	17			

*Significant at < 0.05% level; ** Not significant, $R^2 = 0.9867$, $R^2_{adj} = 0.9717$, Std. Dev.= 3.50, Mean=55.45, C.V= 6.30, Adeq Precision=22.519.

The regression models of the DE % and COD % responses were confirmed by the correlation coefficients of R^2 and R^2_{adj} values using Equations 5.1 and 5.2. For the model, the R^2 and R^2_{adj} values were 0.9847 and 0.9676 for the DE % compared to 0.9867 and 0.9717 for the COD %, respectively. A very important step in the analysis of the results is the check on the adequacy of the model, where a good adequacy indicates that the model is close to the real process (Körbahti et al. 2008). This can be expressed by comparing the actual and the predicted results of the DE % and the COD %, where R^2 gives the reduction in the variability of the response due to the effects of the factors in the modelled process. A higher value of R^2 is not always good, where the desired R^2_{adj} that is also used for the model is not always higher. The results of R^2 and R^2_{adj} indicate that there was a good adequate approximation of the model with the actual values that resulted from the experiments (Körbahti et al. 2009).

The effects of factors (pH of the solution, calcination temperature, and solar intensity) on the response surface and the contours of the degradation efficiency are presented in Figure 5.4. These graphs help to explain the interaction between all the factors in optimizing the conditions so as to maximize the required response. The effects of the pH of the solution and the calcination temperature were semi-spherical, in which the DE % increased at a pH of 6.0 and decreased when the pH was lower or higher than 6.0. However, the degradation efficiency increased when the calcination temperature was decreased to 400°C as shown in Figure 5.4 (a). The effects of the pH of the solution and the solar intensity under the optimum calcination temperature at 400 °C are given in Figure 5.4 (b). The degradation efficiency increased sharply from a minimum to a maximum intensity of 10 - 20 W/m² for cloudy and sunny days, respectively. At the same time, a higher efficiency was found at a pH of 6.0 (optimum value) for all solar intensities compared with the pH values ranging from 4 to 8. Figure 5.4 (c) shows the effects of the calcination temperature and solar intensities on the degradation efficiency. An increase in the degradation efficiency was observed with an increase in the solar intensity and a decrease in the calcination temperature. Additionally, the same sequences for the effects of the factors were obtained for the chemical oxygen demand (COD %) in all the experimental results as shown in Figure 5.5.

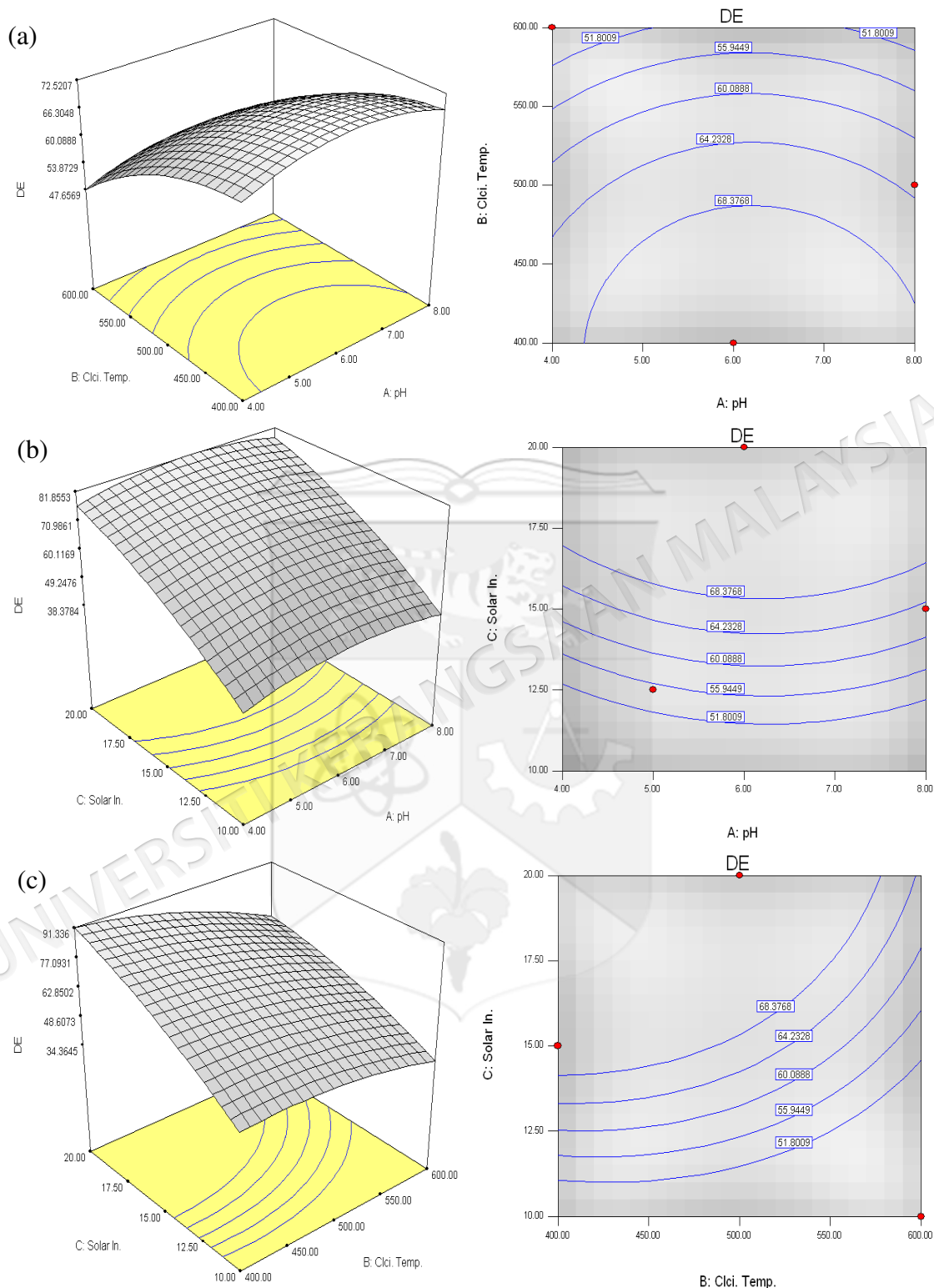


Figure 5.4 Response surface and contours graphs of degradation efficiency (DE %) with affecting of the process factors, (a) calcination Temperature and pH, (b) solar intensity and pH, (c) solar intensity and calcination Temperature.

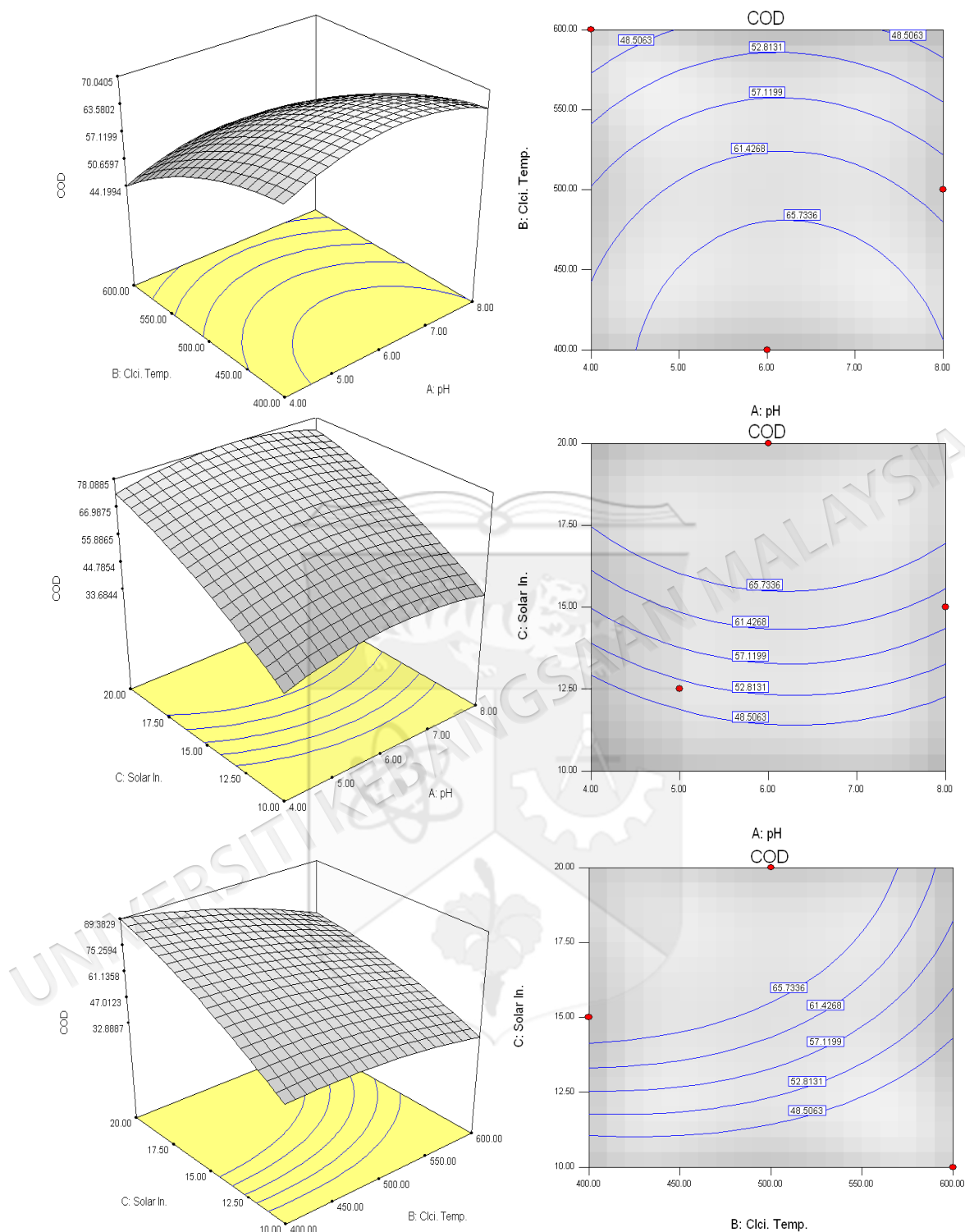


Figure 5.5 Response surface and contours graphs of degradation efficiency (COD %) with affecting of the process factors.(a) calcination Temperature and pH,(b) solar intensity and pH,(c) solar intensity and calcination Temperature.

According to the results from the model, the optimum conditions for the maximum degradation efficiency were created when all factors were under the range of levels. The optimum values for all the factors from the model were generated to produce the maximum values for the DE % and COD % and were coded as the first run in Table 5.8. To validate the process model, the experiment was run under the same values of the predicted conditions for all the factors. A good agreement between the DE % and COD % for the actual values with the predicted values were observed.

Table 5.8 Experimental run and optimum conditions of all factors under range to maximize DE % and COD % for 2-CP.

Run	pH	Calcination temperature (°C)	Solar intensity (W/m ²)	DE% (Predicted)	COD % (Predicted)	DE% (Actual)	COD % (Actual)
1	6.08	404.29	19.76	90.430	88.356	93.47	88.98
2	6.09	411.50	23.00	97.803	95.581	99.54	97.57

To further validate the process model, the second run was applied and adjusted with all the factors under the range when the solar intensity was 23 W/m². This intensity value was measured between 12.00 p.m. to 2.30 p.m. to investigate the effects under real conditions and to determine the best time to achieve the maximum DE%. The highest DE% was found to be 97.803 % compared to 99.54 % from the experiments with a higher removal of COD%. The best time to run all the experiments on the photocatalytic degradation process was between 12.00 p.m. to 2.30 p.m. because the solar intensity then was at its higher value. Further discussion about the effects of solar intensity was noted in the next section of the experiment. The degradation efficiency of 2-chlorophenol under the optimization conditions was confirmed by the HPLC and UV analysis as shown in Figure 5.6. A single peak of the HPLC and UV analysis was obtained at the retention time of 11.2 minutes and wavelength of 274 nm, respectively for 50 mg/l before the degradation reaction in the presence of the ZnO NP. After 60 minutes of exposure to direct solar radiation for the first run of optimization, that peak was decreased based on the percentage of degradation compared to the second run of the experiment as presented in Figure 5.6 (b) and (c).

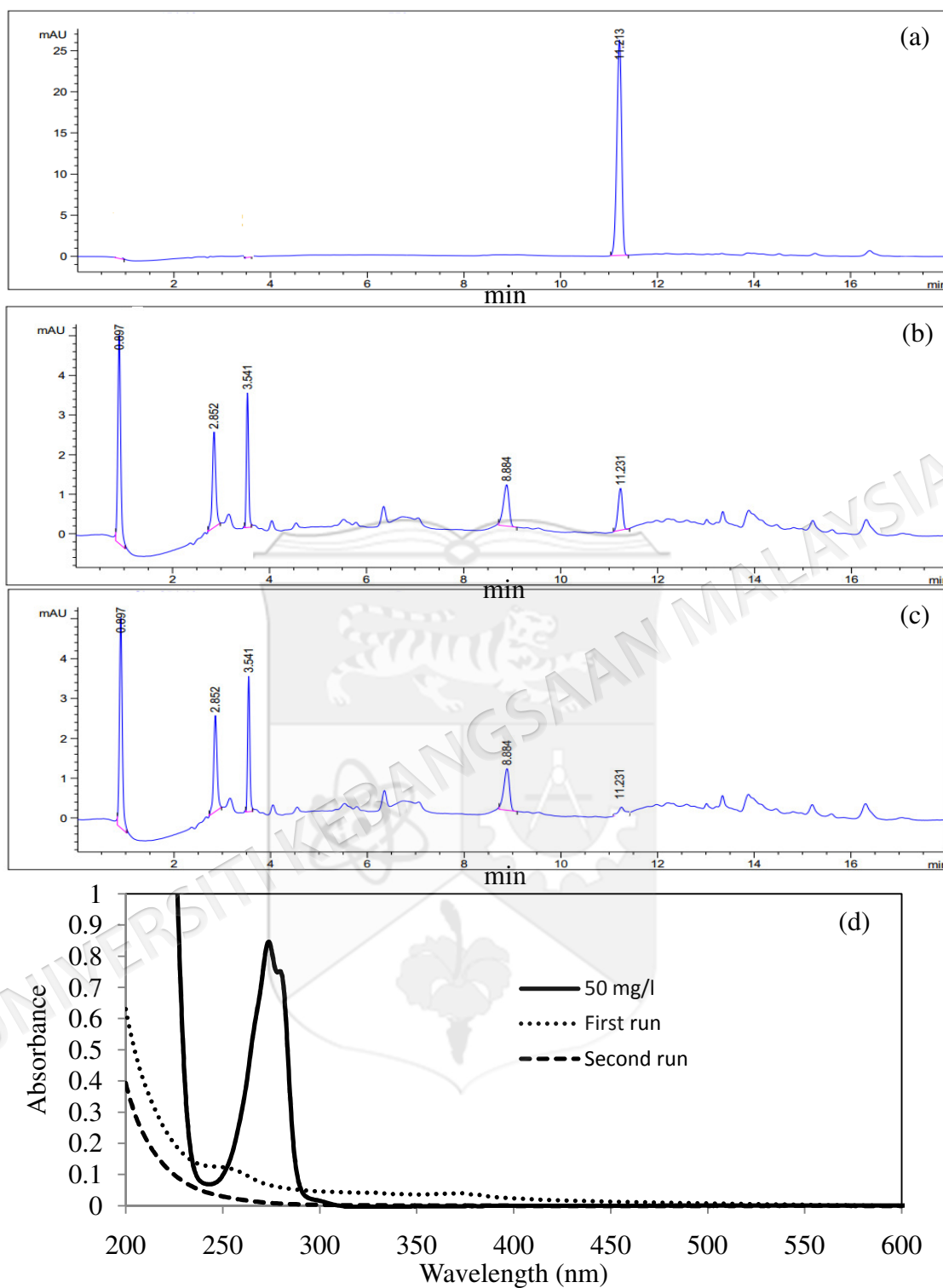


Figure 5.6 Analysis of photocatalytic degradation using HPLC and UV (a) 2-CP before reaction, (b) first run by HPLC, (c) second run by HPLC, (d) first and second run by UV.

These results were confirmed by spectrophotometry. At the same time, the optimization condition for the second run was applied for the 2,4-DCP and 2,4,6-TDCP and the results were 97.5% and 85 % with COD removal of 95% and 82 %, respectively as shown in Figure 5.7. From these results of optimization based on the D-optimal design, the optimum conditions for producing the highest degradation efficiency were a pH of about the middle at 6.0, calcination temperature at a minimum of 400°C and solar intensity at a maximum of 23 W/m². At the same time, these results were discussed in the experimental section to explain why their values were optimum. Finally, the RSM based on the D-optimal design showed an appropriate design for the photocatalytic degradation of chlorophenols under direct solar light. The final model of the process indicated highly accurate predicted values compared to the experimental results, and this may be of help in the development of the process in the industrial field for further economic applications in the future.

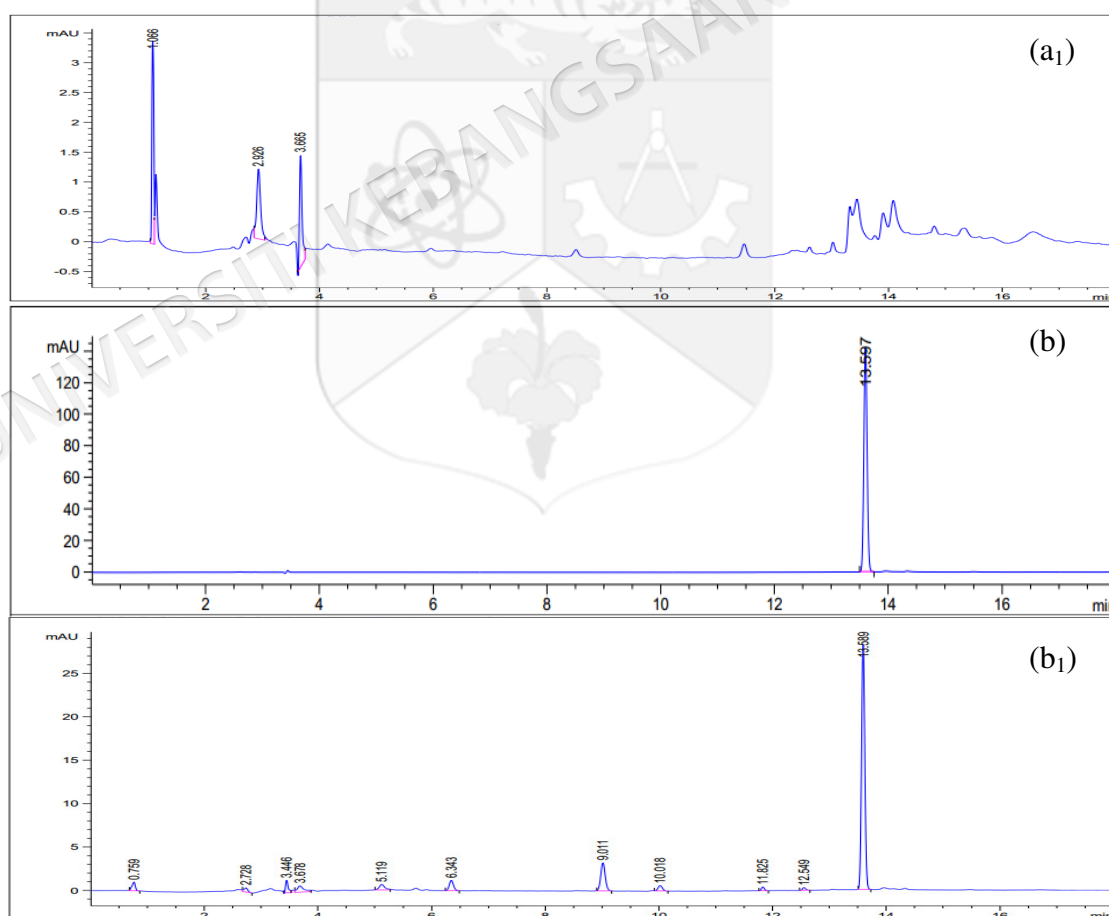


Figure 5.7 Analysis of photocatalytic degradation using HPLC under second run condition (a, a₁) 2,4-DCP, and (b, b₁) 2,4,6-TDCP before and after degradation.

5.2 APPLICATION OF ZnO AND DOPED ZnO NP FOR DEGRADATION OF CHLOROPHENOLS UNDER DIRECT SOLAR LIGHT

5.2.1 Effects of Process Parameters on Activity of ZnO NP

The activity of the synthesized ZnO NP by sol gel method under optimization conditions of parameters was tested for degradation of chlorophenols in water sample. The 2-chlorophenol (2-CP), 2,4-dichlorophenol (2,4-DCP) and 2,4,6-trichlorophenol (2,4,6-TCP) were selected for this study. These compounds have been reported as toxic and difficult to remove by biological method even in low concentration (Veschueren et al. 1983). Last decade, the degradation of chlorophenols using heterogenous photocatalyst as example of advanced oxidation processes (AOPs) shows a total degradation of the toxic compounds under ambient conditions (Gaya et al. 2008). Generation of reactive radical ($\text{OH}^\bullet$) have higher oxidation potential when the photocatalyst absorb the energy of band gap. These reactive radicals ($\text{OH}^\bullet$) leads to degrade many organic pollutant without any toxic of final product (Ahmed et al. 2011). To make the study more economical and useful, the effect parameters such as loading of ZnO NP, initial concentration, pH of solution, type of chlorophenols and ions type doped ZnO NP were optimized. Additionally, to complete economically way of the process, all experiments runs under direct solar radiation and effects of solar intensity was investigated. A discussion and explanation of all parameters effects on degradation efficiency (DE %) which include all factors of screening and response surface of optimization process were presented. To investigate of process parameters effects on activity of ZnO NP an HPLC, GC-MS, UV-vis, IC, COD and AAS instruments were used. Moreover, the toxicity test was evaluated before and after degradation using *E-coil* bacteria.

A. Effects of solar intensity

The photocatalysis has been clarified as one kind of solar technology since 1990 (Malato et al. 2002). The photocatalytic reaction rates relationship is proportional to solar intensity with indicates the rate of reaction limited by the intensity (Ram et al. 2011).

The higher solar intensity between 20-30 W/m² (0.2-0.3 mol photons m⁻² h⁻¹) has been reported for the UVA wavelength of 300-400 nm (Malato et al. 2002). Many researchers confirm that higher activity causes to excess photogenerated species such as e⁻, h⁺, OH[•] and O₂^{-•} (Ahmed et al. 2011). Average solar intensities of UVA and UVB under different weather conditions such as cloudy, semicloudy and sunny day were monitored and recorded using by Skye lynx. Figure 5.8 (a & b) shows the values of UVA and UVB for cloudy, semicloudy and sunny day at time between 10:00 a.m. to 4:00 p.m. At the same time, the average of total solar radiation was measured by Pyranometer and the value given in Figure 5.8 (c).

Based on Figure 5.8, higher values for both average of intensity (UVA and UVB) and total solar radiation, on sunny day compared to cloudy, semicloudy was observed. Effects of solar radiation under different conditions for degradation of chlorophenols were carried out using 50 mg/l of 2-CP, 2,4-DCP and 2,4,6-TCP between time of 11.00 a.m. to 2.30 p.m with ambient temperatures between 28 and 38°C. These experiments were applied under optimal conditions of pH solution of 6.0 and loading of ZnO NP of 2 g/l and the results were depicted in Figure 5.9. The highest degradation efficiency on sunny day was achieved within 60 min for all chlorophenols which compared with the cloudy and semicloudy days in Figure 5.9.

This results attributed to the higher energy absorbed by the ZnO NP which leads to generate more e⁻, h⁺, OH[•] and O₂^{-•} to enhance of reaction rate (Ahmed et al. 2011). Decreasing efficiency from semicloudy to cloudy day due to decreasing light intensity and energy absorbed in which had resulted to lower rate of reaction compared to sunny day. If the sunny condition were to replace by light source as in the industrial processes, more than 2.5 times of degradation efficiency would be obtained when compared during the cloudy day (Poulios et al. 1999). These results are clearly shown in Figure 5.9 for comparison between sunny and cloudy day results.

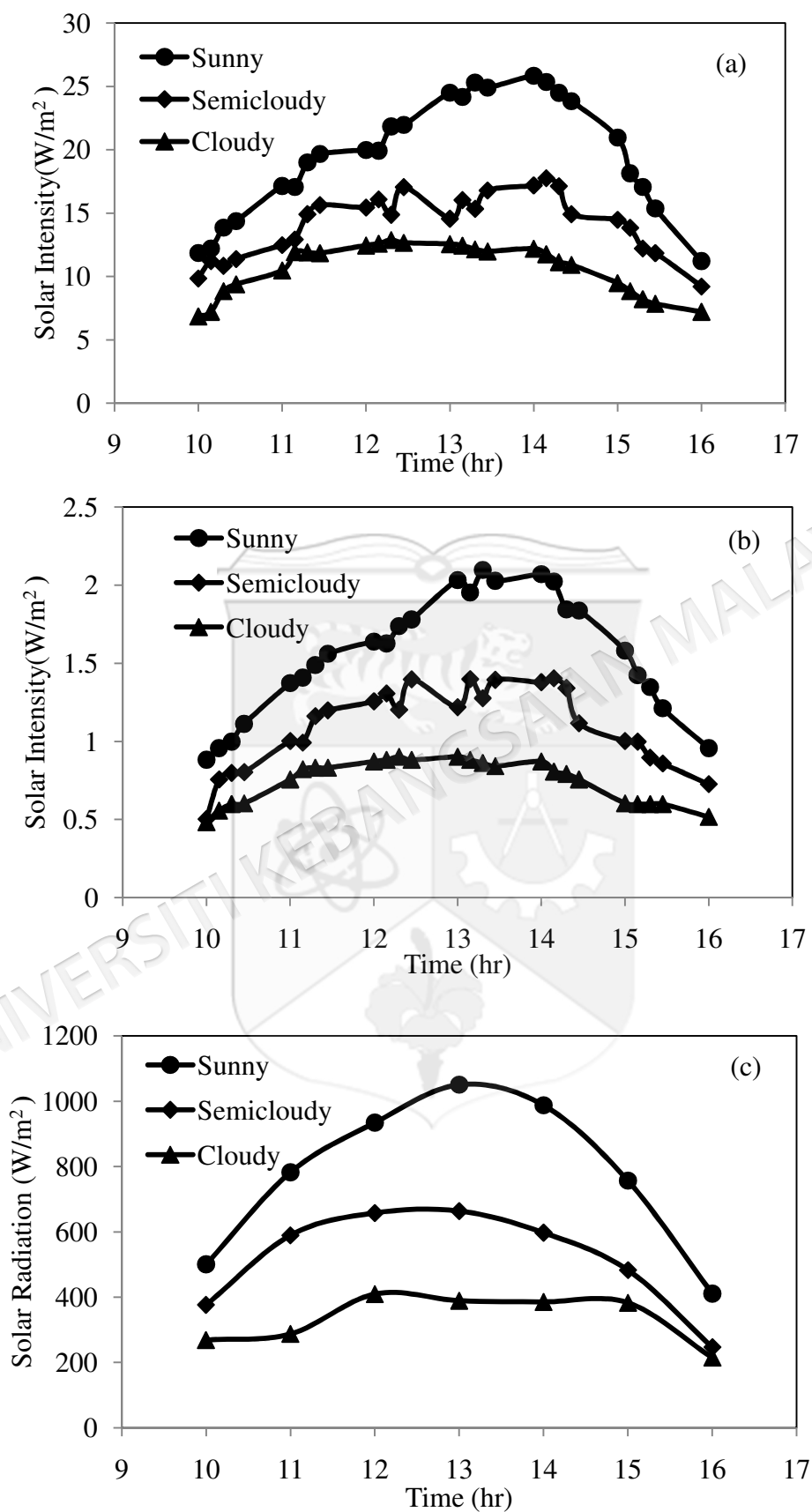


Figure 5.8 Solar radiation measurements (a) UVA, (b) UVB and (C) Total radiation.

Hence, the degradation of the pollutant from water under solar irradiation on sunny day shows enhancement of efficiency of up to 2–2.5 times higher compared to the artificial irradiation (using lamp) (Poulios et al. 1999; Pardeshi & Patil 2008). For this advantages of solar radiation on sunny day as higher photon energy (including UVA and visible), the free cost and environment friendly is the choice to conduct an experiments as the advantage of this study.

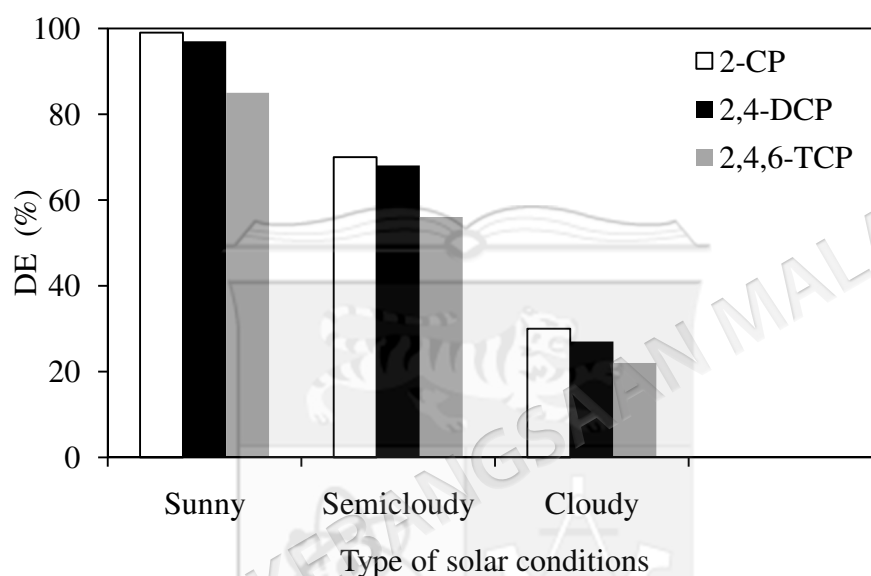


Figure 5.9 Effects of different conditions of solar on degradation efficiency of chlorophenols using initial concentration 50 mg/l, loading of 2 g/l, pH solution at 6.0.

B. Effects of optimization conditions of ZnO NP

The optimization process of the synthesized ZnO NP indicates affected by change of the particle size, surface area and optical properties on efficiency of chlorophenols photocatalytic degradation. Figure 5.10 shows efficiency of chlorophenols using different molar ratio, pH and calcination temperatures under similar conditions of initial concentration of 50 mg/l, pH 6.0, and optimum loading of 2g/l and sunny day. Higher degradation efficiency by 1:2 ratio was achieved because it was the optimum molar ratio as obtained from the synthesis process, which higher surface area, small size and higher optical property were found. Lower efficiency was achieved at mole ratio of 1:1 due to decrease of surface area affecting agglomeration.

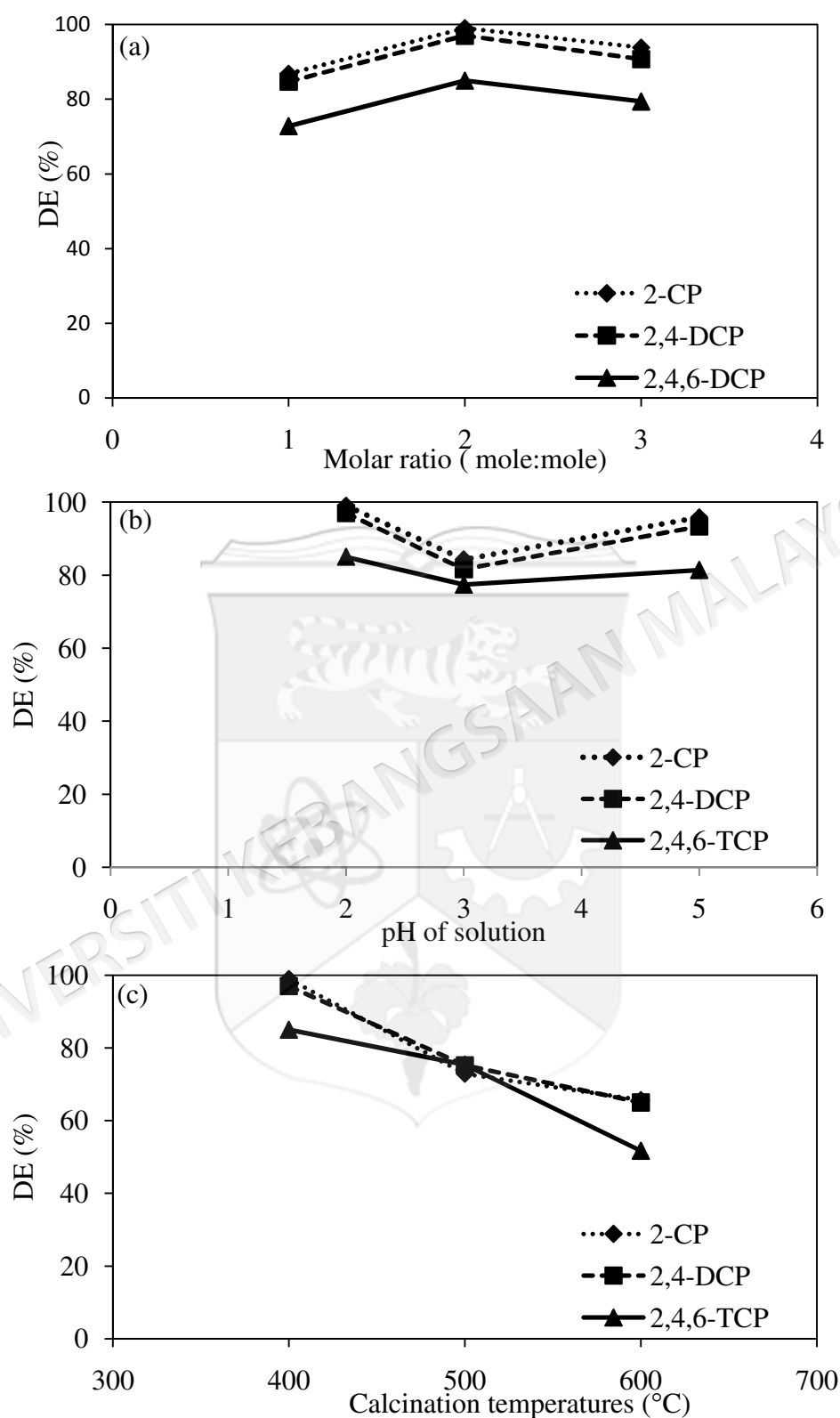


Figure 5.10 Effects of ZnO NP synthesized parameters on degradation efficiency of chlorophenols, (a) molar ratio , (b) pH, (c) calcination temperatures under 60 min irradiation time.

At the same time, increasing efficiency with ratio of 1:3 compare the 1:1 was obtained due to increases of surface area as given in Table 4.14. However less agglomeration of 1:3 ratio were observed which attributed to increasing of surface area more than ratio of 1:1. These results of significant affects on efficiency by surface area were confirmed by the morphologies of catalyst surface using FESEM and TEM (section 4.5.1). An effect of pH on degradation efficiency of chlorophenols in same the sequence of molar ratio which in optimum of pH at 2.0, the highest efficiency was achieved. Decreasing of efficiency at pH 3.0 with slight increase pH 5.0 compared with pH 2.0 because the size was influenced on surface area as observed from XRD, FESEM and TEM analysis.

The calcination temperatures indicates the more significant factor on surface area of catalyst which show a liner decreasing in catalyst efficiency as temperature change from 400 to 600 °C. The bigger particle and pore size of ZnO NP have been reported as main reason for decreases of surface area within calcination process (Seetawan et al. 2011). Degradation efficiency decreases when calcintion temperature increases from 400 to 600°C due to surface area decreased resulting in lower molecules of chlorophenols adsorbed on surface of ZnO NP. These results confirms that values of physical properties such as decreases of surface areas with particle and pore sizes increased were in the same sequence of results recorded using XRD ,FESEM, TEM and UV analysis for parameters optimization (section 4.5.1).

C. Effects of ZnO NP loading

An effect of ZnO NP loading on degradation efficiency was carried out in slurry type reactor (non-concentrating solar reactor) with range of 1 to 3 g/l under sunny day. The optimum loading is important on the effective parameters to avoid higher cost and design of reactor. The efficiency of degradation increases with increasing of ZnO NP loading up to optimum of 2-CP, 2,4-DCP and 2,4,6-TCP as shown in Figure 5.29. The rate of reaction increases with loading due to the active sites more available to degrade more molecules on the surface of the ZnO NP catalyst. When the loading is more than the optimum value, the active sites decreases because the aggregation of particles occurred. However, the scattering light by higher suspension of ZnO particles was

also observed. The relationship between the loading of catalyst and light penetration has been reported earlier (Chen & Ray 1999). The effects of chlorophenols type on optimum loading of ZnO NP was found to be of 2 and 1.5 g/l for 2-CP, 2,4-DCP and 2,4,6-TCP respectively. The decrease of the loading with Cl group in phenol ring was observed as given in Figure 5.11. A 2-CP, 2,4-DCP indicated that almost same optimum loading with decreases for 2,4,6-TCP which may attributed to the geometry of adsorption on the surface of ZnO NP within degradation process. Same degradation efficiency of 2-CP, 2,4-DCP indicated the behavior of adsorption mechanism on ZnO surface as perpendicular (Hilal et al. 2008).

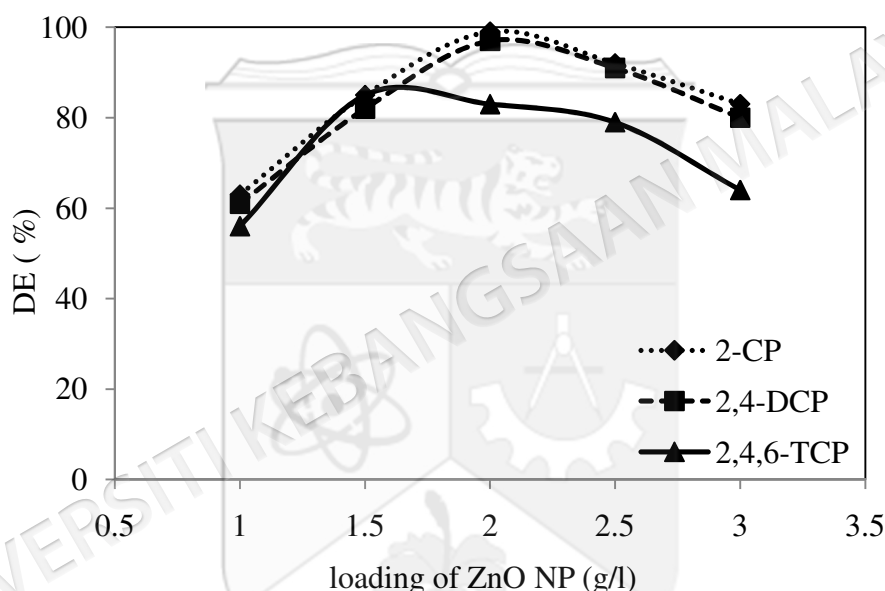


Figure 5.11 Effects of ZnO NP loading on degradation of chlorophenols under pH solution of 6.0, initial concentration of 50 mg/l, and irradiation time of 60 min.

From observations of 2,4,6-TCP efficiency, the adsorption on the surface of ZnO via Cl atoms may attribute to increases in the electronegativity of Cl atom in the phenol ring (Czaplicka et al. 2006). This phenomena leads to adsorption of 2,4,6-TCP as layer (molecule over molecule) on surface of ZnO which may attributed to decreasing degradation efficiency of 2,4,6-TCP compared to 2-CP and 2,4-DCP. At same time, layers of 2,4,6-TCP molecules and higher concentration of ZnO particles beyond the optimum causes a decreasing UV light reached to ZnO surface. This can be main reason to large reduce in efficiency compared to 2-CP and 2,4-DCP. On

adding a Cl atom in phenol rings, the C-Cl bond length decreases with number of Cl atom increased in which to break of this bond became harder as reported earlier (Tan et al. 2010). This observations also shows that lower loading of ZnO for 2,4,6-TCP compared phenol, 2-CP and 2,4-DCP have been reported in Table 2.8.

D. Effects of pH solution

A significant affects of pH solution on efficiency of photocatalytic degradation process under optimum conditions were carried out in wide range pH namely 4.0-10.0. An effect of pH solution on degradation efficiency by interactions of electrostatic charge between the ZnO NP surface and chlorophenols was investigated. The adsorption of chlorophenols on ZnO NP surface also influences by pH which have extremely affected the photocatalytic reaction occurring on ZnO NP surface. A pH reported data on pH varied from 4 to 10 is not workable in industry due to an economical process on the aspect of additional cost (Ram et al. 2011).

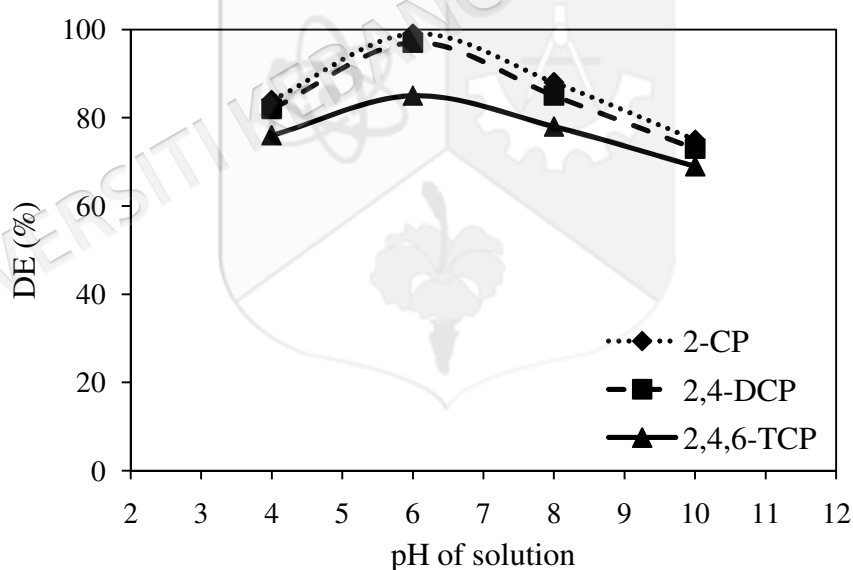


Figure 5.12 Effects of pH solution on the degradation of chlorophenols efficiency under initial concentration of 50 mg/l, irradiation time of 60 min, and loading of 2g/l on sunny day.

It is observable that the size of ZnO NP influences by the solution pH which at zero point charge no interactive rejection to separate particles in aqueous solution. Therefore, aggregation of particles has affected the light absorption as reported earlier

(Ram et al. 2011). Furthermore, changes of pH solution within the photocatalytic degradation process by releasing of acid should be taken into account may has affect on the performance of the process. Figure 5.12 shows the affects of pH solution on the chlorophenols degradation with range of 4 to 10 under optimum condition of solar intensity and loading of ZnO NP.

The chlorophenols exists as anions (negative charge) when the solution pH lower than pKa value of 8.52, 7.8 and 6.23 for the 2-CP, 2,4-DCP and 2,4,6-TCP respectively. Similar affects on degradation efficiency of 2-CP and 2,4-DCP were found under several pH which attributed to the closed pKa value. Therefore, this property leads to same charge of 2-CP and 2,4-DCP molecules (negative charge) into the surface of ZnO NP. A decreasing efficiency on 2,4,6-TCP degradation compared to 2-CP and 2,4-DCP was observed because the lower of pKa (weak negative charge) than them which caused to decrease in the adsorption between the molecules of 2,4,6-TCP and ZnO NP surface. Generally, pH_{zpc} of ZnO is 9.0 was found in this study which the surface was positive below pH_{zpc} while negative at pH higher than pH_{zpc} . The higher degradation efficiencies of all chlorophenols were achieved at pH 6.0 as the optimum pH while decreased when more or less than this value. According to the pH_{zpc} , these results showed that the ZnO NP surface show more positive at pH 6.0 while chlorophenols were negative ($pH < pKa$) which causes to adsorbed chlorophenol molecules on the ZnO surface. At pH of 8.0 which is higher than the optimum pH, the efficiency decreases due to the value of pH closed to the pKa of 2-CP and 2,4-DCP and pH_{zpc} of ZnO. These observations indicated that adsorption of molecules on ZnO NP surface was decreased. Higher decreasing efficiency was obtained. When pH more than 8.0 which may be due to closed value to pH_{zpc} of ZnO and other parameters have affected such as aggregation of particles then decreases of light absorption (Gaya et al. 2008).

Consequently, 2,4,6-TCP indicated lower efficiency under all pH values compared to 2-CP and 2,4-DCP due to the pKa almost similar to pH 6.0. The optimum values of pH to achieve the highest degradation efficiency of phenol, 4-Nitrophenol and polychlorophenols (CP, DCP and TCP) has to be in the range 5.0 to 7.0 as been reported by many studies using ZnO presented in the literature review listed in Table

2.8. In the case of 2,4,6-TCP, of efficiency was not only influenced by pH but the geometry of adsorption on ZnO surface also has negative effect. In general, decreasing of degradation efficiencies when the pH solution less and more optimum were observed because amphoteric nature of ZnO which dissolved as Zn^{2+} ions at less than 4 and formed zincates such as $\text{Zn}(\text{OH})_4^{2-}$ at higher value of 10 (Evgenidou et al. 2005).

E. Effects of initial concentration

The initial concentration of pollutants has been reported as one of important process plays main role to determine the final efficiency of photocatalytic process. Increasing the pollutant concentration leads to absorb more molecules at the surface of catalyst which affected on the rate of degradation (Krishnakumar & Swaminathan 2010). An effect of initial concentration of chlorophenols on degradation efficiency was carried out using concentration range of 25 to 150 mg/l under optimal conditions at pH 6.0, loading of 2g/l and sunny day. Before photocatalytic reaction start, the adsorption-desorption equilibrium was performed under dark condition for 60 min. Figure 5.13 shows the amount chlorophenols adsorbed on the ZnO NP surface within 60 min stirred under dark condition.

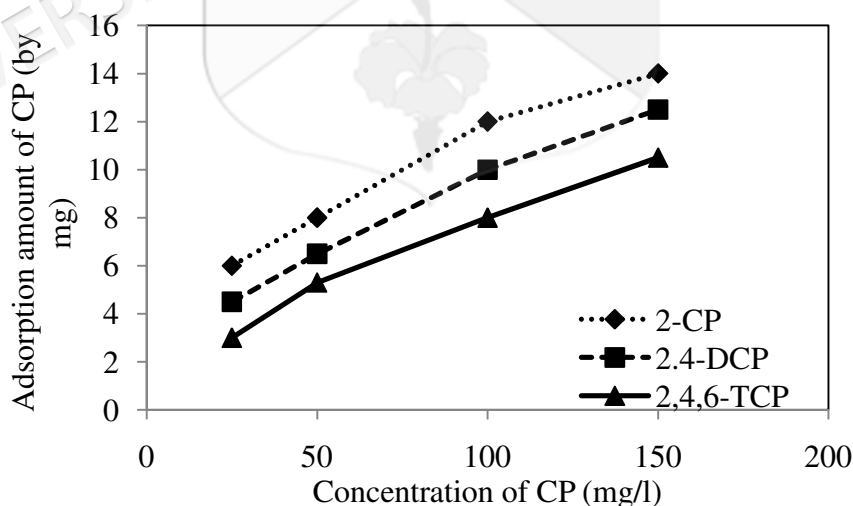


Figure 5.13 Comparison of adsorption amount of chlorophenols on surface of ZnO NP under dark condition for 60 min.

For all types of chlorophenols, the adsorbed amount increased from the 25 to 150 mg/l due to molecules available under high concentration. The adsorption decreases with increasing Cl group in phenol ring of each concentration of 2-CP, 2,4-DCP and 2,4,6-TCP. These results may attributed to the polarity and other properties of 2-CP, 2,4-DCP and 2,4,6-TCP (Czaplicka 2006). After the adsorption-desorption equilibrium was investigated and then reactor containing chlorophenols with dispersion of ZnO NP was exposed to solar light to start photocatalytic reaction. A photocatalytic degradation of chlorophenols was performed under same condition pH 6, loading of 2 g/l and sunny day with time exposure from of 12.00 to 2.30 p.m. Figure 5.14 shows the degradation efficiency as function of the irradiation time for all chlorophenols in which increases of degradation with prolong time of exposure. At same time, degradation efficiency decreased when concentration of chlorophenols increased from 50 to 150 mg/l due to availability of more molecules on surface of ZnO during the time of degradation. Therefore, relative number of reactive radicals ($\cdot\text{OH}$ and $\cdot\text{O}^{2-}$) to attack of chlorophenols molecule became less (Pardeshi & Patil 2009). Moreover, increasing the concentration of chlorophenols leads to virtually masking the surface of ZnO and preventing the photons interacting with ZnO which decreases of degradation rate (Behnajady et al. 2006). It is noteworthy that the degradation of chlorophenols depends strongly on the initial concentration.

The $\text{Cl}\cdot$ radical formed during process of chlorophenols decomposition react with the conduction band electron or hydroxyl radicals to generate chloride anion and hypochlorous acid which leads to reduce the degradation rate as reported earlier studies (Rauf et al. 2008). Lower concentration of 2-CP and 2,4-DCP exhibits higher percentage of degradation in which achieved within 60 min. A higher concentration namely 100 to 150 mg/l needs around 120 to 180 min for complete of degradation as shown in Figure 5.14 (a,b). Slight difference of degradation between the 2-CP and 2,4-DCP may attributed to slight increases of the chloride anion concentration of 2,4-DCP (Gaya et al. 2008). However, decreasing efficiency of the 2,4,6-TCP degradation not only due to increasing chloride anion but other factor such as intermediates compound from fragmentation of 2,4,6-TCP have been reported earlier (Huang et al. 2005; Czaplicka 2006).

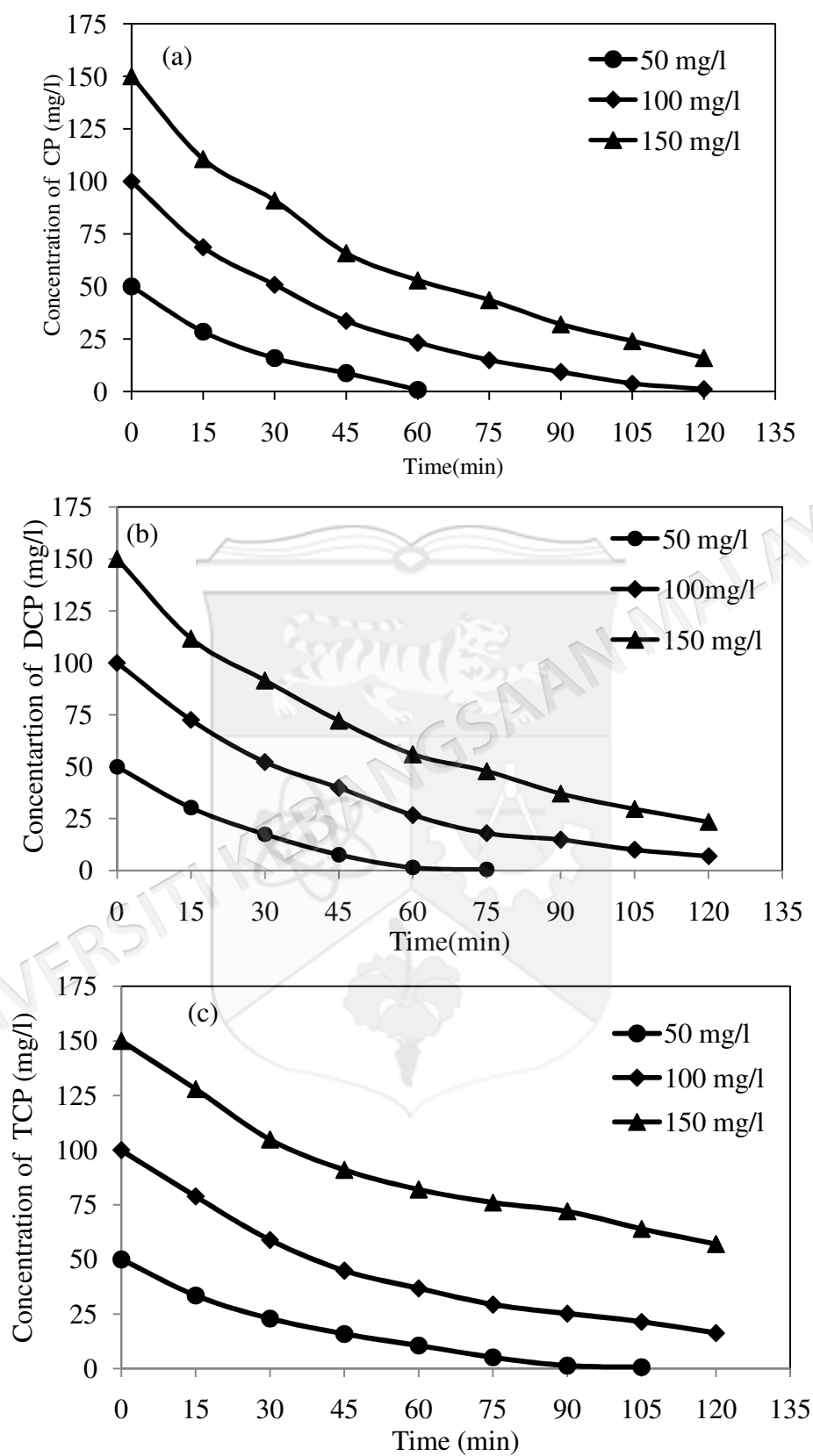


Figure 5.14 Photocatalytic degradation of different chlorophenol concentrations under optimum conditions (a) 2-CP, (b) 2,4-DCP, (c) 2,4,6-TCP.

The degradation of 2,4,6-TCP to 2-CP and 2,4-DCP have been identified as intermediates compound which leads to decrease of degradation rate. Hence, a 50 mg/l as initial concentration was selected to be an optimum concentration to study the effects of other parameters such as pH, calcinations temperature and solar intensity on photocatalytic degradation efficiency of chlorophenols. The kinetic of photocatalytic degradation process is depends on initial concentration and type of chlorophenols have been reported by Vialaton et al. (2002). Chlorophenols degradation seems a first order reaction in aqueous solution as shown in Figure 5.15 and reported earlier by Czaplicka et al. (2006).

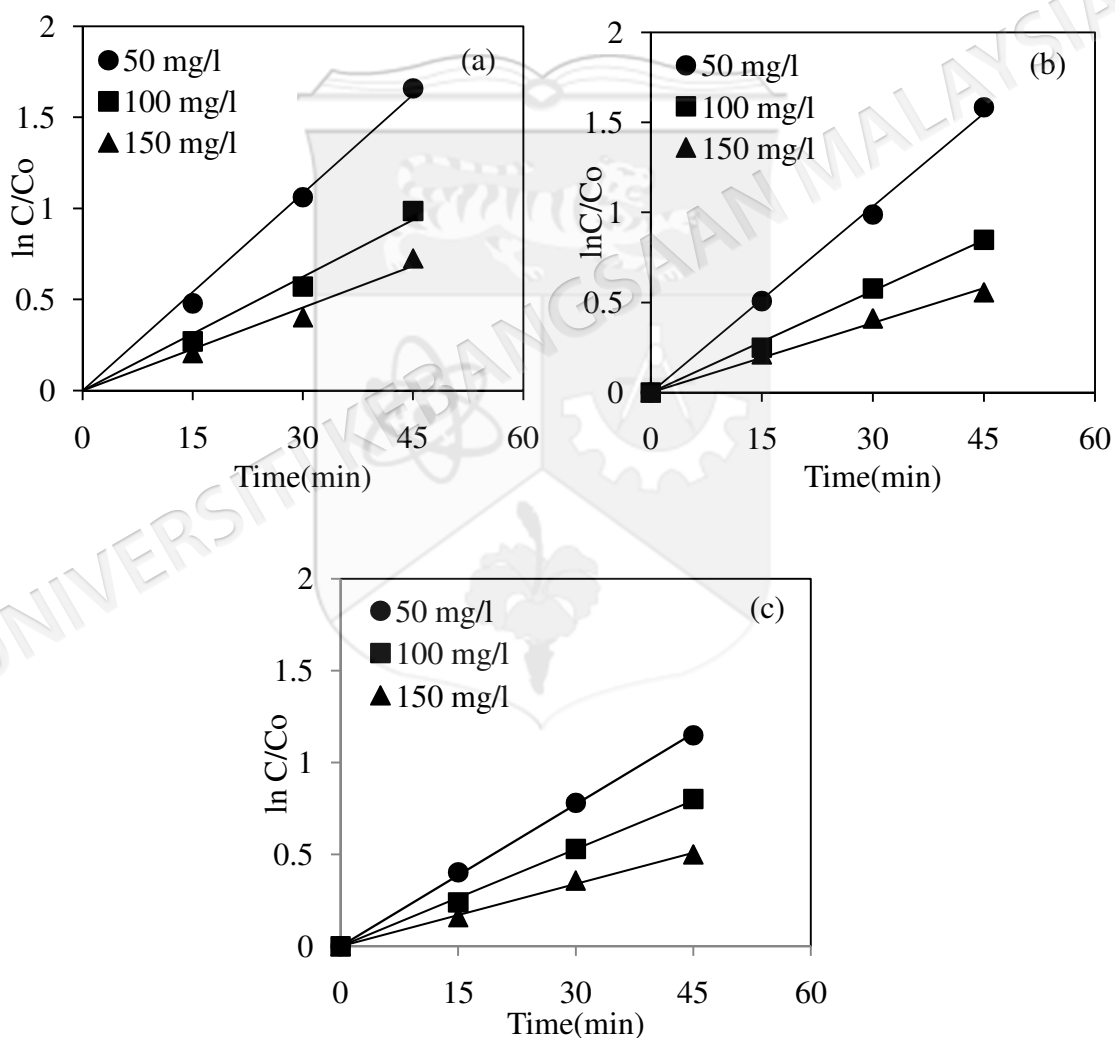


Figure 5.15 The first order reaction of (a) 2-CP, (b) 2,4-DCP, (c) 2,4,6-TCP

The photocatalytic degradation of chlorophenols using ZnO NP follows pseudo-first order kinetics with a rate expression given by:

$$\ln\left(\frac{C_0}{C}\right) = kt \quad (5.3)$$

where k is the rate constant, and C_0 and C are the concentrations at time $t = 0$ and t , respectively. The kinetic results of photocatalytic degradation showed a linear fit to the pseudo-first order reaction rate constant k values calculated at various concentrations based on the slopes of the curves and listed in Table 5.9.

Table 5.9 First-order rate constants of chlorophenols at different initial concentrations.

Concentration mg/l	2-CP		2,4-DCP		2,4,6-TCP	
	k, min ⁻¹	R ²	k, min ⁻¹	R ²	k, min ⁻¹	R ²
50	0.0361	0.9926	0.0344	0.9976	0.0258	0.9997
100	0.0208	0.9718	0.0188	0.9969	0.0171	0.9966
150	0.0152	0.9592	0.0129	0.9914	0.0106	0.9863

The overall rate constants indicates that the reaction is faster at low concentration of chlorophenols which may attributed to higher surface of ZnO NP to adsorb more molecules and generate a reactive radicals of $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ as reported for heterogenous photocatalysis process (Anandan et al. 2007). A decreasing rate with increases of chlorophenols concentration was observed due to more molecules cover the surface of ZnO NP and then the formation of reactive radicals may be decrease. The rate constant decreases with the increasing Cl group in phenol ring from 2-CP to 2,4,6-TCP.

The chlorophenols removal was investigated within the photocatalytic degradation process using chemical demand oxygen (COD) measurement. The removal percentage of all chlorophenols was in sequence with the degradation efficiency as shown in Figure 5.16. Increased COD (%) removals with increasing irradiation time were recorded for all chlorophenols at several concentrations. This

result confirms that degradation process decreases when concentration of chlorophenols increased. The COD removal of 2-CP and 2,4-DCP at low concentration showed almost same value indicating that higher degradation was taken place. At concentration of more than 50 mg/l, the COD removal decreased due to formation of more intermediate compounds which require more time to degrade. Less removal of COD for all concentrations was observed for 2,4,6-TCP compared to 2-CP and 2,4-DCP under same conditions.

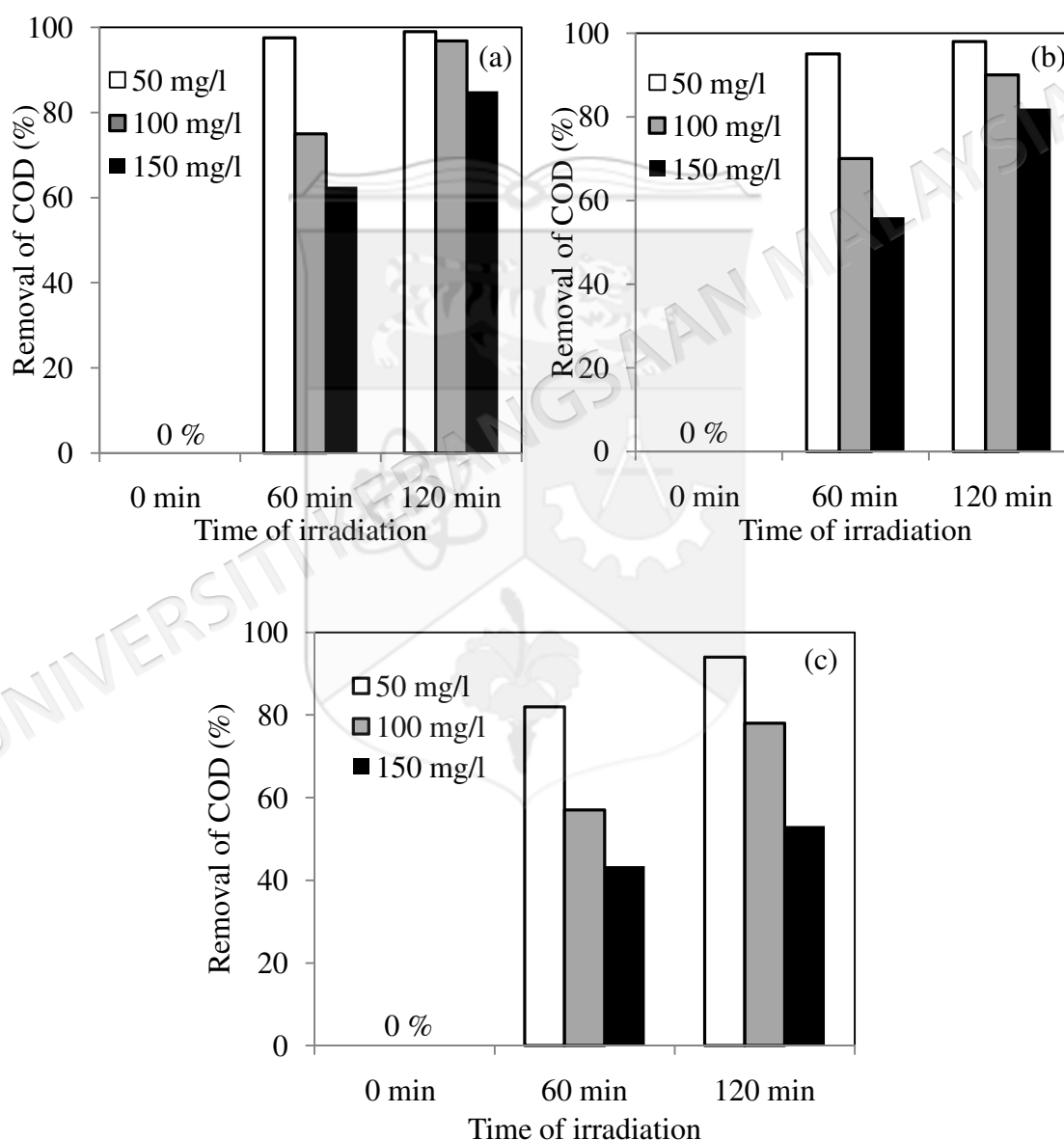


Figure 5.16 Comparison of COD removal of chlorophenols with different concentrations under same conditions, (a) 2-CP, (b) 2,4-DCP, (c) 2,4,6-TCP.

Higher concentration of 2,4,6-TCP shows decrease in COD removal due to the presence of intermediates such as 2-CP and 2,4-DC and needs time to reduce it to lower molecular weight compounds in the lower COD measurement. The COD removal showed the same sequence with the degradation efficiency which was confirmed the removal of toxic compound from water using the ZnO NP in assistance of solar radiation.

F. Effects of chlorine ions

Degradation of chlorophenols using the ZnO and Doped ZnO NP under solar radiation was also investigated by measuring chloride ions (Cl^-) as shown in Figure 5.17. The effects of degradation rate of chlorophenols in presence of chloride ions have been summarized as below:

- (i) The degradation reaction were carried out at pH 6.0 below pH_{pzc} , where the chloride ions (Cl^-) attached to the surface of ZnO NP because positively charge. However, the chloride ions competed with chlorophenols for active sites which leads to decreasing of degradation rate (Gaya et al. 2009).
- (ii) Presence of chloride ions aqueous solution acts with the electron compared to oxygen. This step decreases superoxide radical formation as oxidation agent which reduces hydroxyl radical formation. Then the efficiency of degradation decreases as the chloride ions increases. The inhibition of $\cdot\text{OH}$ and $\text{O}_2^{\cdot-}$ radicals formation through the following reactions was explained below:



These reactions are undesirable as the presence of chloride ions limits the activity of the ZnO NP catalyst. The hypochlorous acid (HOCl), which is a weak acid formed by dissolving chlorine in water, slightly decreases the pH value from 6.0 to 5.3 with all concentrations of 2-CP, 2,4-DCP and 2,4,6-TCP increased from 50 to 150 mg/l (Czaplicka 2006).

(iii) Reaction between the chloride ions and radicals within the degradation reaction shows decreased probability of reaction between the chlorophenols and radicals which reduced the degradation rate (Alhakimi et al. 2003).

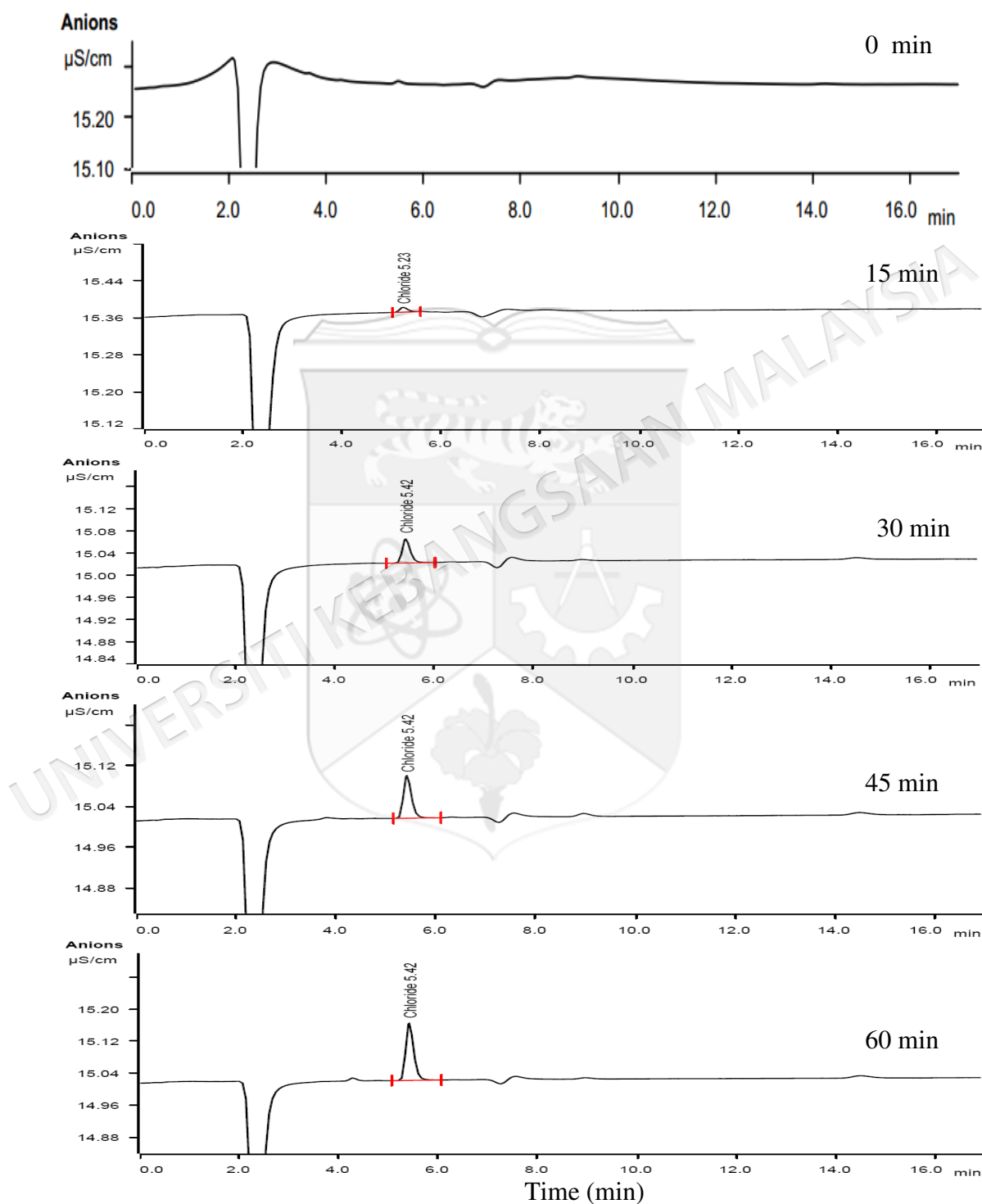


Figure 5.17 Chloride ions increasing as function of irradiation time for degradation process of chlorophenols.

Increasing chloride ions concentration (Cl^-) after degradation of 2-CP, 2,4-DCP and 2,4,6-TCP was observed (Appendix G). Figure 5.18 shows the chloride ions increasing with increased of 2-CP, 2,4-DCP and 2,4,6-TCP concentration from 50 to 150 mg/l under 90 min of irradiation time. However, the chloride ion concentration of 2-CP and 2,4-DCP indicates to be close to each other, which perform to the same influenced on degradation efficiency and rate of reaction. For 2,4,6-TCP, all concentration showed higher chloride ions than 2-CP and 2,4-DCP because three groups of chlorine (Cl) containing phenol ring which attributed to decline of degradation efficiency compare to 2-CP and 2,4-DCP. These results indicates that higher degradation efficiency of 2,4,6-TCP with increasing time of irradiation .

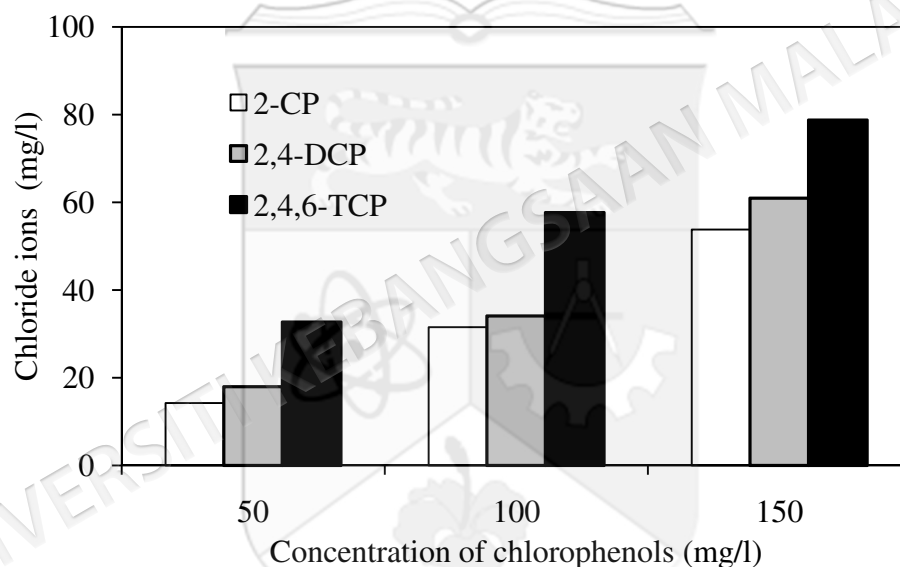


Figure 5.18 Comparison between 2-CP, 2,4-DCP and 2,4,6-TCP for chloride ions production within degradation process.

5.2.2 Effects of Doping on Activity of ZnO NP

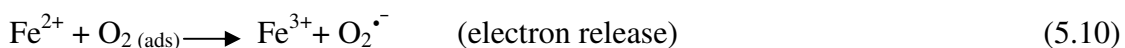
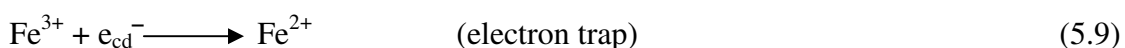
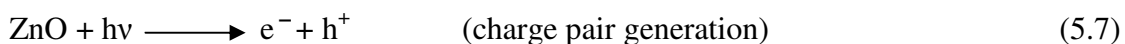
The aim of ZnO NP doping using the metal transition and rare earth of elements in this study to improve the physical and optical properties of ZnO NP as reported previously (Hassan et al. 2012). Physical properties such as surface area and optical such as band gap have been more significant factors effects on activity of ZnO NP for degradation of chlorophenols (Shinde et al. 2011; Shukla et al. 2010). This

enhancement of properties indicates economy issues by reducing the amount of catalyst amount within the photocatalytic process (Sakthivel et al. 2003).

A. Effects of dopants concentration (wt. %)

Photocatalytic activity of ZnO and doped ZnO NP were tested using the 2-CP with initial concentration of 50 mg/l under same experimental condition of pH at 6.0, loading of 1g/l and 60 min of irradiation time. The Fe³⁺, Sm³⁺ and Ti⁴⁺ ions were selected for doped ZnO NP with concentration of 0.25- 1.00 wt.%. It can be observed that the photocatalytic activity increases as all dopants concentration increased as shown in Figure 5.19. However, this activity indicates strong influenced by the surface area and optical properties which increases or decreases of these factors were substituted each other to enhance of degradation efficiency. The maximum value of efficiency was achieved using optimal concentration of dopant, which perform an approximately one and a half times more than undoped ZnO NP. For the Fe³⁺ doped ZnO NP, the efficiency increasing gradually with concentration increase up to optimal of 0.5 wt. % and then decreases as indicated in Figure 5.19 (a). This enhancement of degradation efficiency was due to the shifting the absorbance to the visible region which higher energy supplied (by the decreasing of band gap) (Hassan et al. 2012). A slight increasing of surface area also enhanced the efficiency as reported earlier (Pathak, & Purohit 2013).

Moreover, the excess the Fe³⁺ ions caused to decreasing of degradation efficiency because the amount more than optimal can function as a photo-generated hole and trap. These results showed inhibiting the recombination of hole–electron as described by Zhou et al. (2006) in which summarized by the following equations:



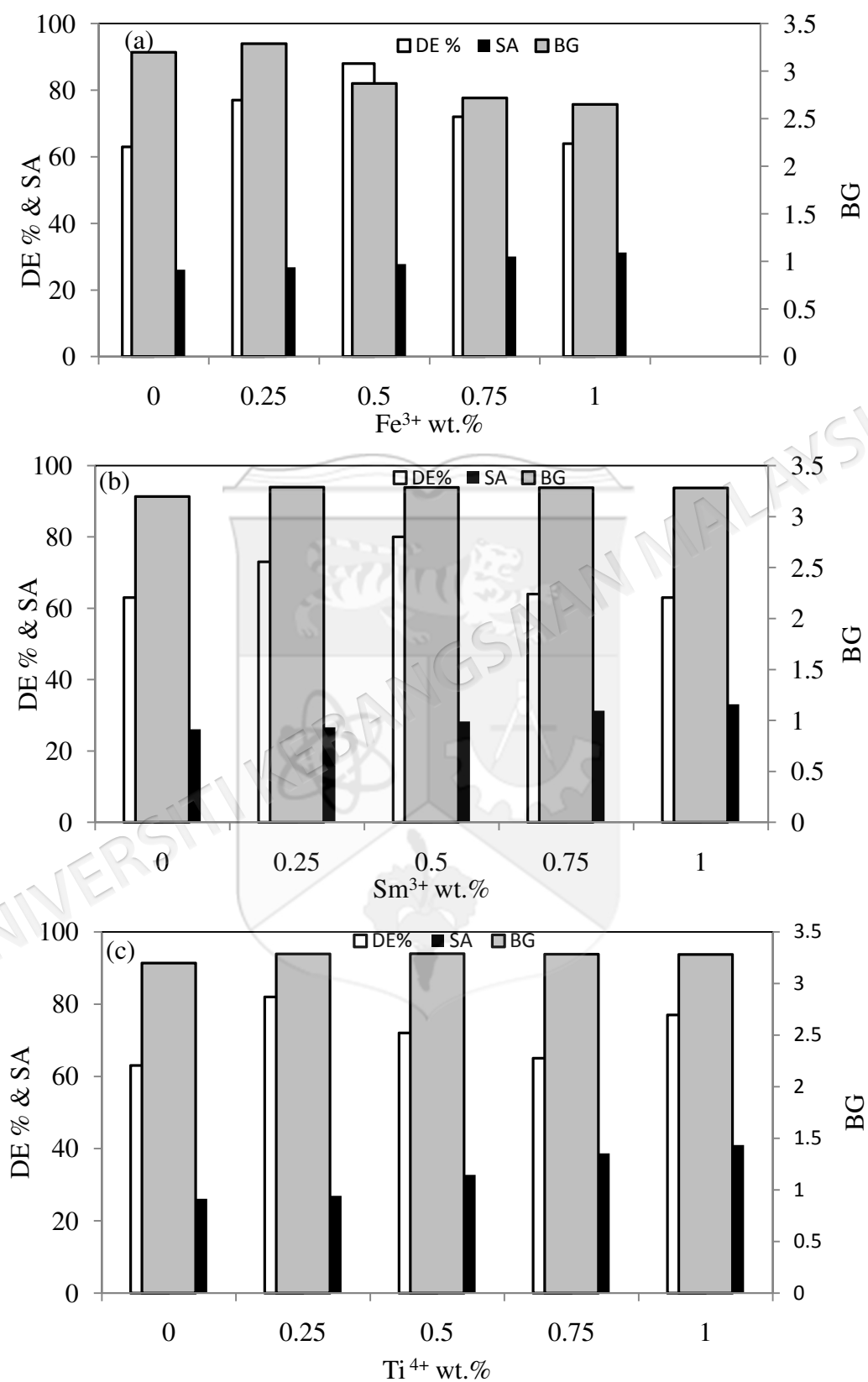


Figure 5.19 Comparison of photocatalytic degradation efficiency (DE %), surface area (SA) and band gap (BG) vs. the different concentration of dopants.

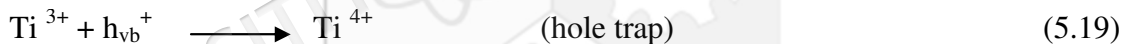
The Fe^{3+} ions react as electron holes and traps which related in the formation of Fe^{2+} and Fe^{4+} (Eq. 5.9 and 5.12). The Fe^{2+} and Fe^{4+} ions are relatively unstable compared with Fe^{3+} ions (Zhou et al. 2006). To regain stability, these ions will react with oxygen and hydroxyl ions adsorbed onto the catalytic surface to produce hydroxyl ($\text{OH}^\bullet$) and superoxide ($\text{O}_2^{\bullet-}$) radicals (Eq. 5.10 and 5.13). The recombination rate was found to be much faster at the optimum concentration of Fe^{3+} ions, which was expected to have the highest catalytic activity as reported by previous studies (Zhou et al., 2006). At higher concentration of Fe^{3+} (> 0.5 wt. %), the availability of traps is reduced because the Fe^{4+} reacts with electrons ($\text{Fe}^{4+} + e^- \longrightarrow \text{Fe}^{3+}$) and Fe^{3+} acts as a recombination center ($\text{Fe}^{3+} + e^- \longrightarrow \text{Fe}^{2+}$ and $\text{Fe}^{2+} + h_{\nu} + \longrightarrow \text{Fe}^{3+}$) thus reducing the activity of the Fe^{3+} doped ZnO photocatalyst.

Figure 5.19 (b) shows the degradation efficiency, surface area and band gap of Sm^{3+} doped ZnO with several concentrations compared to undoped ZnO NP. The efficiency indicates the sequence of Fe^{3+} doped ZnO samples which the optimal at 0.5 wt. % of Sm^{3+} ions. When the Sm^{3+} concentration increases up to 0.5 wt. %, the degradation increased up to a maximum value and then declined with the Sm^{3+} concentration exceeded than optimal. The degradation efficiency by Sm^{3+} doped ZnO showed 80 % which is slightly lower than Fe^{3+} -doped of 88 %. This may due to the band gap almost same with enhancing was occurred in UV region more than visible. However, a slightly increases of surface area compared to Fe^{3+} doped ZnO was not led to higher efficiency which also need to the optimized of Sm^{3+} doping concentration as reported by earlier study (Carp et al. 2004). A small amount of Sm^{3+} ions enhances the activity, which may due to an increase in the separation of the photo generated electrons and the photo generated hole traps (Xiao, et al. 2008). To generate the oxidative species, such as the superoxide radical ion ($\text{O}_2^{\bullet-}$), the Sm^{3+} ions presence on the ZnO surface need to react with the electrons that are transferred to the oxygen molecules, which is almost same mechanism of Fe^{3+} doped ZnO.

The electron-hole recombination is faster in the presence of Sm^{3+} ions, due to the unstable Sm^{2+} ions that can easily transfer electrons to the oxygen molecules (Zhou et al. 2006). When the concentration of Sm^{3+} ions was more than optimal, i.e., > 0.5 wt. %, a decrease in the catalyst activity was observed. This could be attributed to

the excess Sm^{3+} working as a recombination center as illustrated in Eq. (5.12 & 5.13). These reactions have the effect of reducing the photocatalytic activity of Sm^{3+} -doped ZnO when the optimal concentration was exceeded.

Effects of Ti^{4+} ions on the degradation efficiency with same concentration of Fe^{3+} and Sm^{3+} was investigated and given in Figure 5.19 (c). The highest efficiency of degradation was found under lower concentration of 0.25 wt. % of Ti^{4+} . These results indicate that the efficiency of 82 % is slightly more than Sm^{3+} -doped ZnO which attributed to the same of the band gap with enhancement of absorption in UV region more than visible. Gradually decreasing of the efficiency up to concentration of 0.75 wt. % and the increases at 1 wt. % was observed because highest surface area available in compare to other concentration of Ti^{4+} ions (Shinde et al. 2011).



The electrons traps by the Ti^{4+} ions was moved to the surface of catalyst and reacts with adsorbed O_2 to generate reactive super oxide and the hydroxyl radicals. From these equations, Ti^{4+} and Ti^{3+} show the responsible of degradation efficiency was controlled by the generated electron-hole recombination. The efficiency decreases with increased dopant have been reported as the excess amount of ions works as recombination center within the degradation process (Zhou et al. 2006). The increasing efficiency of degradation follows the reaction given in Equations from (5.14) to (5.18) producing more reactive of $\text{OH}^\bullet$ and $\text{O}_2^{\bullet-}$ radicals achieved at surface of Ti^{4+} doped ZnO NP. Similarly, increasing Ti^{4+} ions indicates Ti^{3+} is trapped on hole and converted to Ti^{4+} in which this cycle between electron and hole trap decreased degradation efficiency. In this study, increasing valence of dopants plays significant role in photocatalytic degradation of chlorophenols was observed. The optimal concentration of dopants decreases with valence was increased under range of

0.25 to 1.00 wt. %. Accordingly, the optimal concentration of Fe^{3+} and Sm^{3+} dopants as 0.50 wt. %, while Ti^{4+} as 0.25 wt. % were found from the experimental results of degradation process.

B. Effects of optimal concentration (wt. %) loading

After the optimization test of dopant concentrations (wt. %), loading of catalyst was investigated to avoid using any excess amount to create a more economic process. The loading of catalyst is one of the main factors governing the degradation rate of pollutants with nanoparticles. Generally, effects of loading were evaluated using 1.0 to 2.5 g/l compared to undoped ZnO NP as shown in Figure 5.20. The highest degradation of 2-CP showed by undoped ZnO using 2.0 g/l and then declined when the amount was more than 2.0 g/l as explained previously. The enhancement of degradation by Fe^{3+} , Sm^{3+} and Ti^{4+} was investigated clearly to reduce the amount of catalyst to half and increased of efficiency to one and half times. At low loading of 1.0 g/l for all of 0.5 wt. % Fe^{3+} , 0.5 wt. % Sm^{3+} and 0.25 wt. % Ti^{4+} doped ZnO indicates higher efficiency than undoped ZnO due to the increasing surface area and optical properties (Hassan et al. 2012). The degradation efficiency of 2-CP reduces with increasing doped ZnO loading more than 1.0 g/l because increasing of dopant ions at higher loading works as recombination center which led to reduced the degradation efficiency (Zhou et al. 2006). However, Fe^{3+} was higher efficiency compared to Sm^{3+} and Ti^{4+} doped ZnO under all loading which may attributed to enhance of absorption of visible region of solar spectrum (Aydın et al. 2013; Mishra & Das 2010). Moreover, at all loading shows the degradation efficiency of Ti^{4+} doped ZnO more than Sm^{3+} -doped ZnO due to the slightly increased surface area. However, no more enhances of degradation efficiency with increasing of catalyst loading was observed. These results attributed to the increasing of electrons in conduction band which working as recombination centers (Zhou et al. 2006).

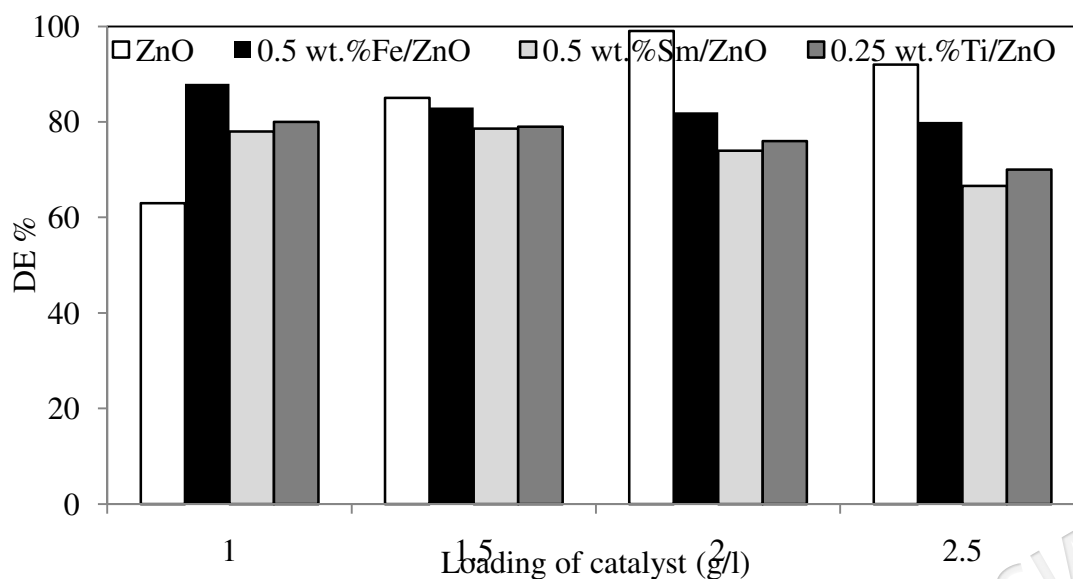


Figure 5.20 Effects of loading on degradation efficiency (DE %) for optimal concentration of Fe^{3+} , Sm^{3+} and Ti^{4+} doped ZnO, with 50 mg/l of 2-CP at pH of 6.0, 60 min irradiation.

C. Effects of initial concentration of chlorophenols (CP)

To evaluate the effects of chlorophenols concentration on all doped ZnO sample activity, a 50 to 150 mg/l of 2-CP, 2,4-DCP and 2,4,6-TCP with solution pH of 6.0 and sunny day were applied for all experiments. The concentration of 0.5 wt. % for Fe^{3+} , Sm^{3+} and 0.25 wt. % for Ti^{4+} doped ZnO with 1 g/l loading were used to test the degradation activity. Accordingly, no change in surface charge of pH_{zpc} behavior (ZnO as 9.1 compared to dopant ZnO as 8.85) which led to same mechanism of chlorophenols adsorption are occurring at the surface. Therefore, clear effects of other parameters such as the surface area and optical properties are playing main role for the activity of catalyst on chlorophenols degradation. To start of photocatalytic reaction after adsorption-desorption equilibrium under dark, the reactor containing of chlorophenols with doped ZnO NP was exposed to solar light. Degradation efficiency decreases with increasing loading of Fe^{3+} doped ZnO NP concentration was observed for all types of chlorophenols as shown in Figure 5.21. These results indicates the limited active site and generating relative number of reactive radicals ($\cdot\text{OH}$ and $\cdot\text{O}^{2-}$) on surface of catalyst which decreasing of chlorophenols molecule attacking during reaction (Pardeshi & Patil 2009).

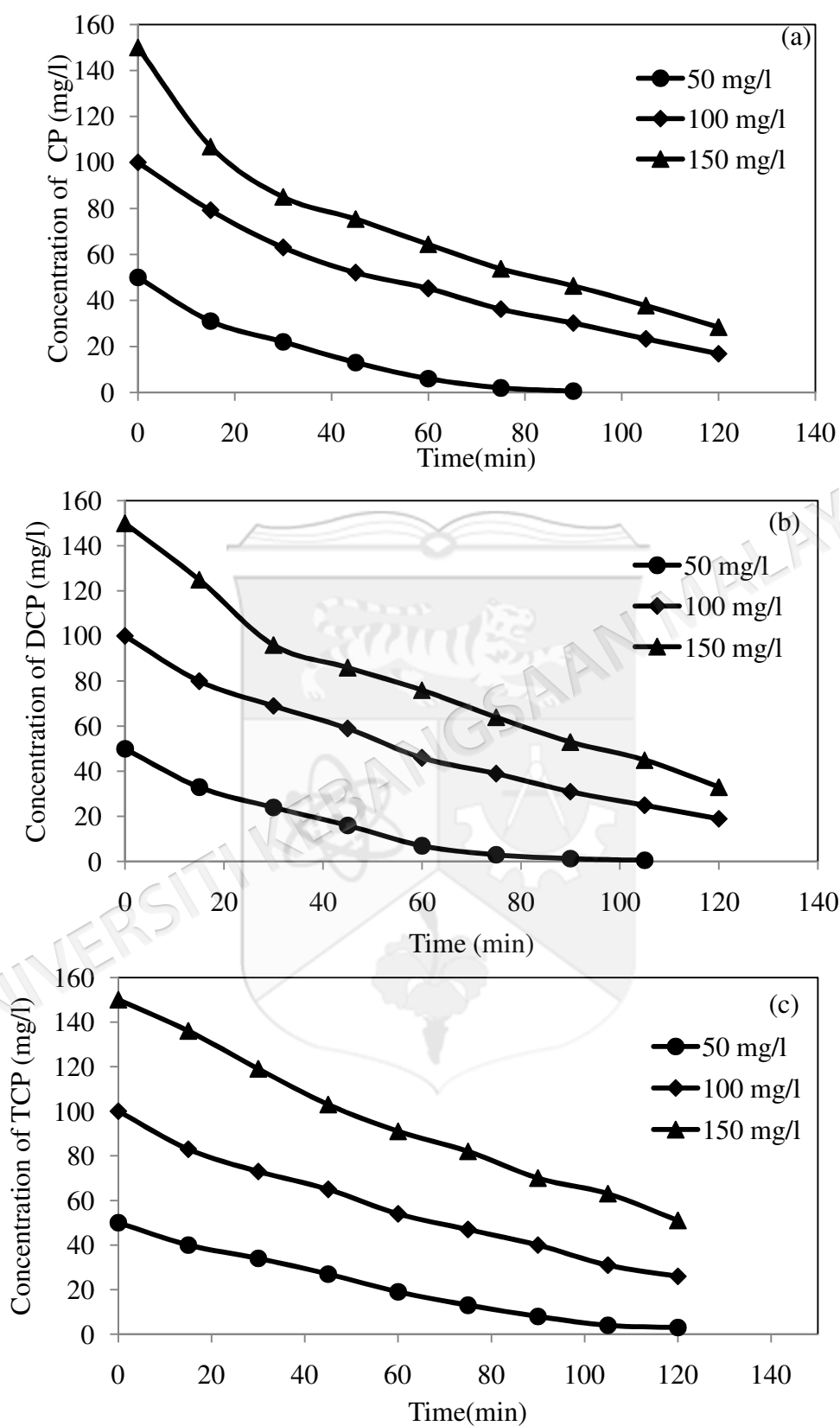


Figure 5.21 Effects of initial concentration of chlorophenols on degradation efficiency (DE %) using of Fe^{3+} doped ZnO, (a) 2-CP, (b) 2,4-DCP and (c) 2,4,6-TCP.

Increasing concentrations leads to virtually masking the surface of doped ZnO preventing the photons interacting with catalyst (Behnajady et al. 2006). The concentration of chloride anion (Cl^-) increases with concentration of chlorophenols. The chloride anion (Cl^-) has reported to reduce the degradation efficiency by the reaction with the $\cdot\text{OH}$ and $\text{O}_2^{\cdot-}$ radicals (Rauf et al. 2009).

The same effect of chloride anion (Cl^-) produced within the degradation process was reported for doped ZnO. At lower concentration of 2-CP and 2,4-DCP shows higher degradation efficiency achieved within 90 min. Slight difference of degradation between 2-CP and 2,4-DCP may attributed to slight increases of the chloride anion concentration of 2,4-DCP compared to 2,4,6-TCP. Degradation of all chlorophenols using Fe^{3+} , Sm^{3+} and Ti^{4+} doped ZnO indicated that kinetic of photocatalytic reaction is a first order reaction as reported earlier (Czaplicka et al. 2006). It is noteworthy that the degradation of chlorophenols depends strongly on the initial concentration. The optimal concentration of dopant (0.5 wt. % for Fe^{3+} , Sm^{3+} and 0.25 wt. % for Ti^{4+}) showed that close results for degradation of chlorophenols with different concentrations. Activity of Sm^{3+} and Ti^{4+} doped ZnO for degradation of different chlorophenols concentration was reported in Appendix H.

5.2.3 Toxicity Evaluation of Chlorophenols Degradation

Degradation of chlorophenols using ZnO and its doped NP under solar light were confirmed by the toxicity test. The toxicity of chlorophenols before and after degradation process using optimal conditions of synthesis of ZnO NP and parameters of process were evaluated. However, doped ZnO samples by optimal concentration of Fe^{3+} , Sm^{3+} and Ti^{4+} also compared to undoped ZnO. *Escherichia coli* (*E-coli*) bacteria were used as indicator strain and growth inhibition to determine the level of chlorophenols toxicity before and after degradation (Wahab et al. 2010). For toxicity test, the agar disk diffusion method was applied as a good method as reported in the earlier study to reflect the toxicity levels of chlorophenols (Milner and Goulder, 1986). Firstly, about 10 μl of chlorophenols with different initial concentration of 50 to 150 mg/l was dropped to the sterilized paper disc on the surface of agar to determine the chlorophenols toxicity. Figure 5.22 shows the different zones inhibition of chlorophenols toxicity according to type of chlorophenols and concentration. The

zones increases with increasing initial concentration were observed for all chlorophenols of 2-CP, 2,4-DCP and 2,4,6-TCP. At same time, that zones of inhibition increased in order of 2-CP < 2,4-DCP < 2,4,6-TCP at all concentrations which have been reported earlier (Milner & Goulder 1986). The toxicity of chlorophenols depended on the concentration and number of Cl group and their positions in the ring of phenols (Milner & Goulder 1986).

The values of zone inhibition of *E-coli* using different concentration and type of chlorophenols were summarized in Table 5.10. These values of inhibitions indicated higher toxicity of chlorophenols before degradation using ZnO and it doped ZnO NP catalyst under solar radiation. After 120 min of irradiation time using pure ZnO NP with 2g/l, the inhibition zone was decreased to smaller area for all 2-CP concentrations because almost all chlorophenols were converted to nontoxic by-products such as CO₂ and some acids (acetic and oxalic acids) (Czaplicka et al. 2006). Moreover, lower inhibition indicates by the 2-CP and 2,4-DCP compare to 2,4,6-TCP which due to close of degradation efficiency. Higher inhibition zone of 2,4,6-TCP within the same time of irradiation compare to 2-CP and 2,4-DCP for all concentrations was observed. These results attributed to the fragments of 2,4,6-TCP within degradation to 2-CP and 2,4-DCP which were investigated by HPLC and GC-MS. Generally, the toxicity of chlorophenols (higher chlorinated) is indicated by increasing lipophilicity that results to higher potential of uptake into the organism. This phenomena leads to inhibition of bacteria growth (proliferate) with increasing inhibition zone as reported by Czaplicka et al. (2006). Moreover, Fe³⁺ doped ZnO shows that slightly difference of zone inhibitions compare to ZnO NP at lower concentration (50 mg/l) of 2-CP, 2,4-DCP and 2,4,6-TCP. However, the inhibitions increases with higher concentration (100 and 150 mg/l) which attributed to decreasing degradation efficiency compared to ZnO 1 g/l was used for 120 min irradiation time. However, Sm³⁺ and Ti⁴⁺ doped ZnO resulted similar inhibition zone due to the slight difference of degradation efficiency of all chlorophenols. Smaller zone of inhibition was observed after degradation chlorophenols with lower concentration (50 mg/l) by ZnO and doped ZnO NP. These results attributed to those effects of acetic acid as final by-product on *E-coli* growth as reported earlier (Roe, et al. 2002). However, the

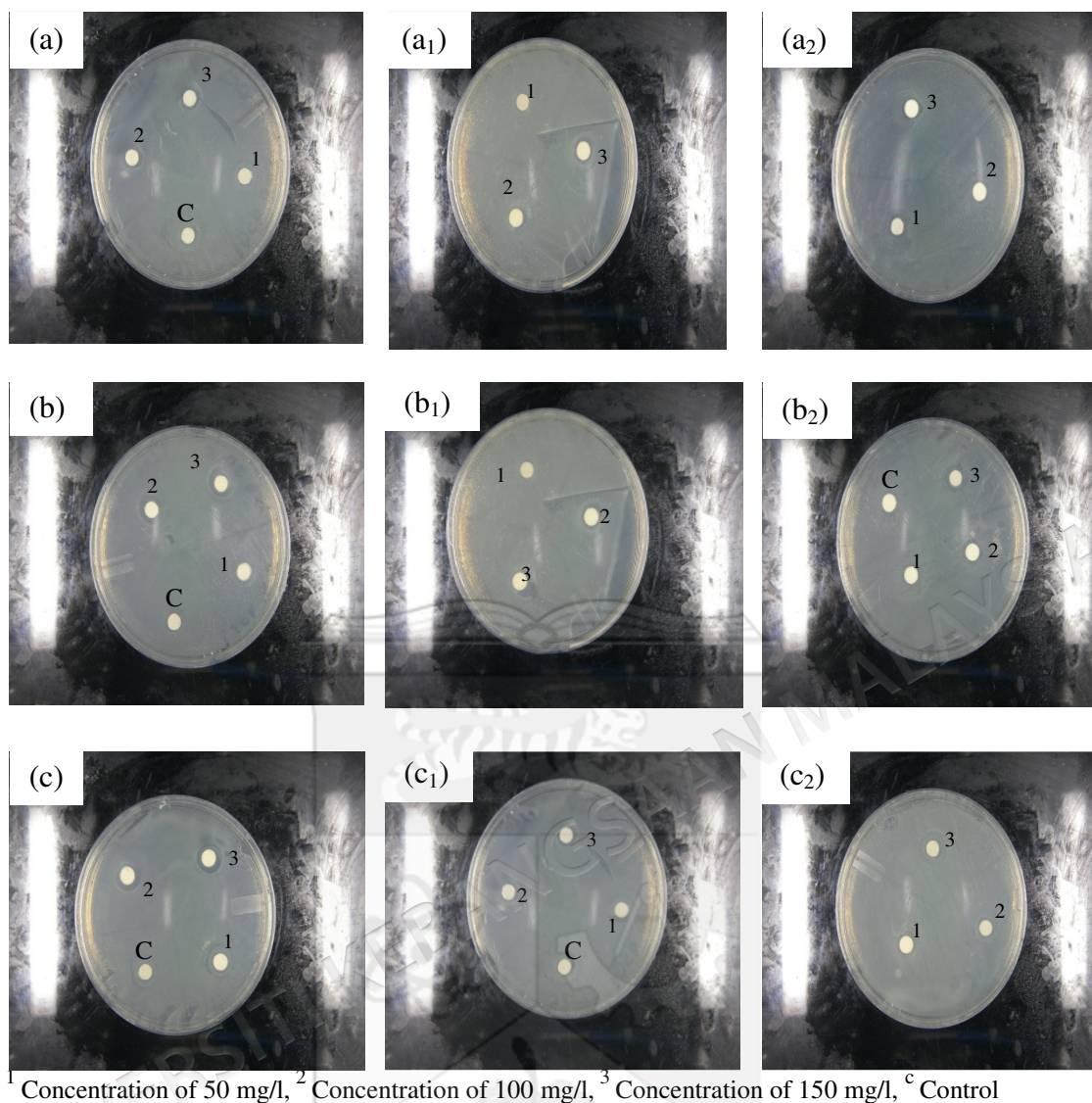
presence of acetic acid after chlorophenols degradation using ZnO and doped ZnO NP was investigated by HPLC and GC-MS analysis.

Table 5.10 Comparison of toxicity of chlorophenols (by mm) before and after degradation time using ZnO and it doped by Fe^{3+} ions under optimal concentration.

Catalyst	CP			DCP			TCP		
	50 ^a	100 ^b	150 ^b	50 ^a	100 ^b	150 ^b	50 ^a	100 ^b	150 ^b
None	1.0	1.5	2.2	1.3	1.8	2.7	1.8	2.1	3.0
ZnO	0.25	0.35	0.75	0.3	0.50	1.0	0.55	0.75	1.2
$\text{Fe}^{3+}/\text{ZnO}$	0.35	0.60	1.1	0.40	0.75	1.4	0.75	0.95	1.6

(a=after 60 min, b=after 120 min irradiation time)

The effect of Zn^{2+} ions on growth of *E-coli* bacteria have been reported by many researchers where ZnO largely uses as antibacterial compound (Rekha et al. 2010). The Zn^{2+} ions released by dissolution of ZnO NP have significant influence on growth of *E-coli* bacteria at concentration between 15 to 43 mg/l of Zn^{2+} (Li et al. 2011). In this study, the Zn^{2+} ions were measured by the atomic absorption spectrometer (AAS) and found to be less than 10 mg/l ($> 0.01\%$ based on 2 g/l ZnO) as given in Appendix I. This value indicates the ZnO NP synthesis by sol gel method more stable for degradation process conditions such as the pH and temperature. The doping of ZnO NP using metal transition such as the Fe^{3+} have been showed best way to decreases of ZnO dissolution (Li et al. 2011). After degradation reaction, all Fe^{3+} , Sm^{3+} and Ti^{4+} doped ZnO samples shows that dissolution of Zn^{2+} was reduced in between 2-5 mg/l ($> 0.004\%$ based on 1 g/l doped ZnO). No detection of dopant ions after degradation was found which may attributed to the strong dopant ions bonded in ZnO matrix after substituted the Zn^{2+} (Hassan et al. 2014). All of these observations show that optimization of preparation and process parameters are good for removal of all chlorophenols from water under solar radiation in presence of ZnO and doped ZnO NP.



¹ Concentration of 50 mg/l, ² Concentration of 100 mg/l, ³ Concentration of 150 mg/l, ^c Control

Figure 5.22 Toxicity test of chlorophenols before and after degradation using *E. coli* bacteria, (a) 2-CP before, (b) 2,4-DCP before, (c) 2,4,6-TCP before (a₁); 2-CP by ZnO, (b₁) 2,4-DCP by ZnO, (c₁) 2,4,6-TCP by ZnO; (a₂) 2-CP by Fe³⁺/ZnO, (b₂) 2,4-DCP by Fe³⁺/ZnO, (c₂) 2,4,6-TCP by Fe³⁺/ZnO.

5.2.4 Intermediates Compound of Chlorophenols Degradation

Photocatalytic degradation of chlorophenols by ZnO and doped ZnO NP was investigated to small molecules as intermediate compounds. These compounds were determined using GC-MS as shown in Figure 5.23. The final compounds peaks showed same retention time by HPLC during the degradation and identified by comparison with the standard of commercial compounds as given in Appendix J.

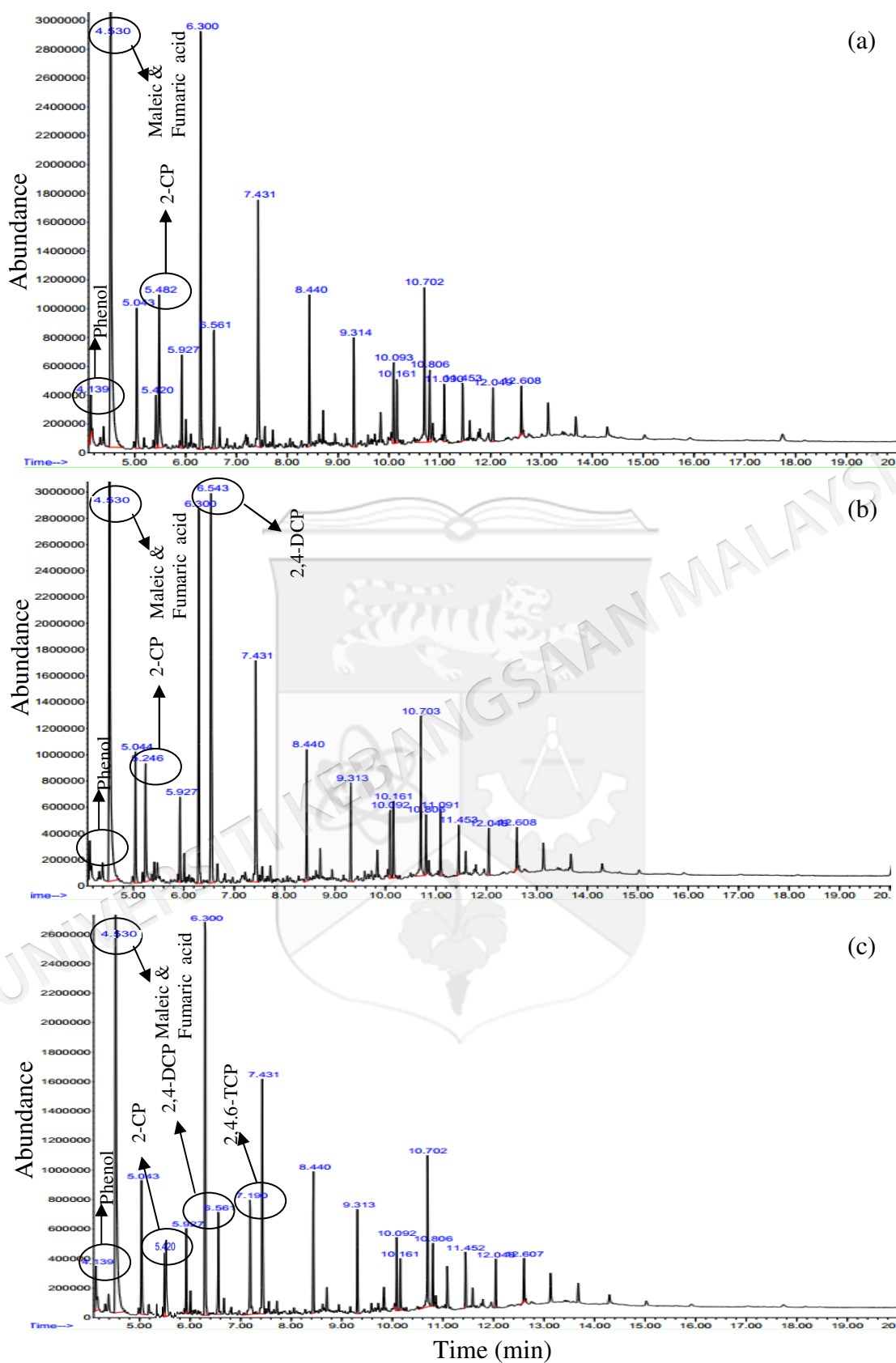


Figure 5.23 GC-MS chromatogram of intermediate compounds within degradation process of (a) 2-CP, (b) 2,4-DCP, (c) 2,4,6-TCP.

Figure 5.24 indicates final compounds of 2-CP (as example) at same retention time of HPLC peaks for ZnO and doped ZnO NP under same experiment conditions. According to HPLC results of all chlorophenols, the acids such as acetic and oxalic acid as final intermediate compound was produced which have been reported by Bandara et al. (2001). The main intermediate compounds for all chlorophenols using GC-MS were found to be phenol, catechol, hydroquinone, chlorohydroquinone (CHQ), hydroxyhydroquinone (HHQ), Carbon dioxide and water which also confirmed by the previous studies (Rao et al. 2003). The main compounds with their retention time were summarized in Table 5.11.

Table 5.11 Comparison of retention time between the HPLC and GC-MS for the chlorophenols and intermediate compounds.

NO.	Compounds Name	Retention Time of HPLC (min)	Retention time of GC-MS (min)	Molecular Weight(g mol ⁻¹)	Amount mg/L
1	2- Chlorophenol	11.2	5.48	128	13.60
2	2,4-Dichlorophenol	12.7	6.54	162	-
3	2,4,6- Trichlorophenol	13.5	7.19	196	-
4	Phenol	8.50	4.139	94	1.64
5	Catechol	5.88	6.72	110	1.09
6	Hydroquinone(HQ)	3.96	6.56	110	0.69
7	hydroxyhydroquinone(HHQ)	-	8.012	127	-
8	2-chlorohydroquinone (CHQ)	-	6.072	145	-
9	Fumaric acid	-	4.53	119	-
10	Maleic acid	-	4.53	119	-
11	Acetic acid	3.41	-	60	4.00
12	Oxalic acid	2.59	5.92	90	4.125

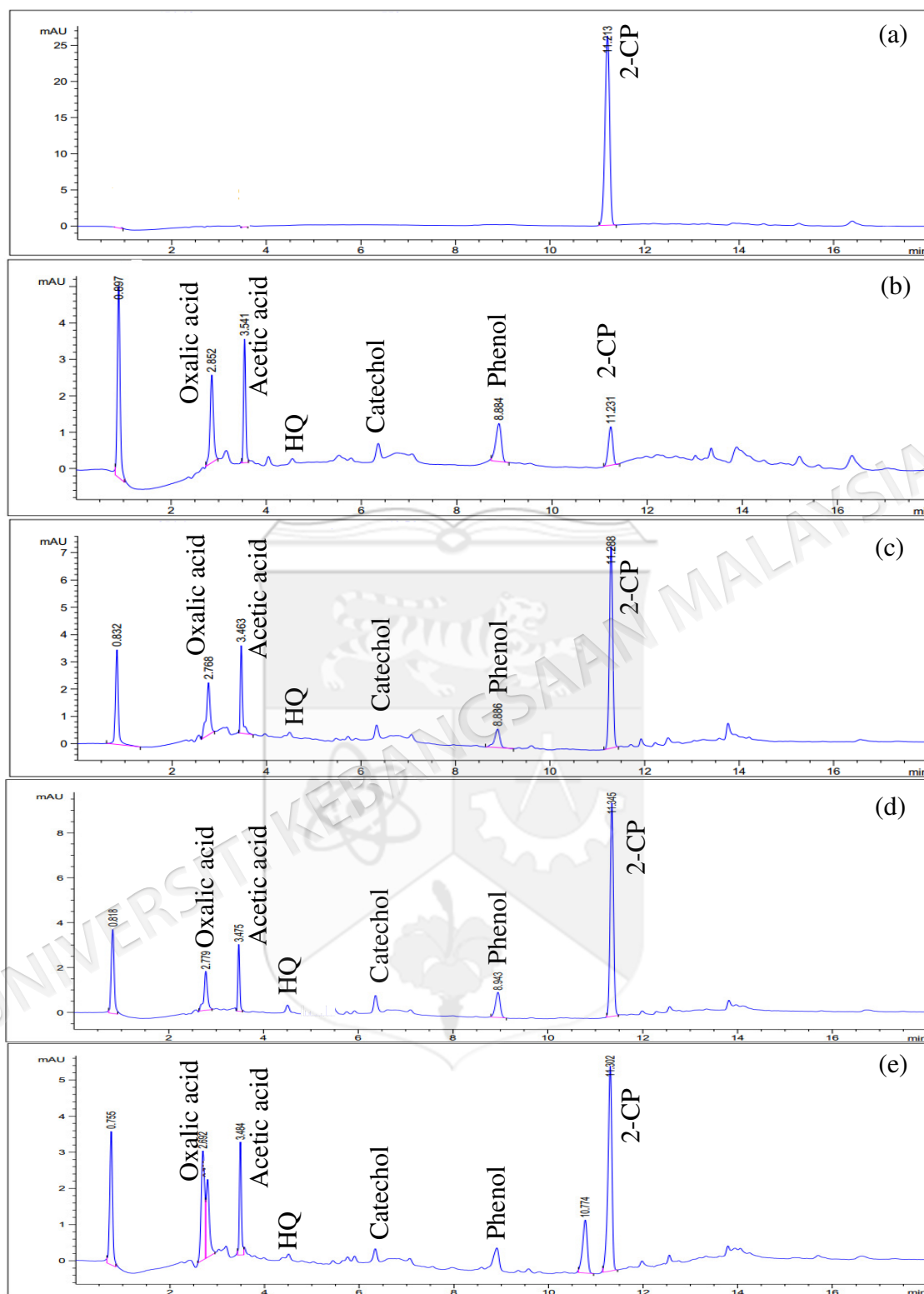


Figure 5.24 HPLC chromatogram of degradation of 2-CP under optimum condition using (a) 2-CP before (b) ZnO, (c) $\text{Fe}^{3+}/\text{ZnO}$, (d) $\text{Sm}^{3+}/\text{ZnO}$, (e) $\text{Ti}^{4+}/\text{ZnO}$.

Figure 5.25 shows the GC-MS chromatogram for intermediate compounds were same with HPLC as given in Table 5.11. All of the characteristic masses (m/z) of chlorophenols and intermediates were in agreement with molecular weight of their compounds. At the same time, characteristic masses (m/z) of hydroxyhydroquinone (HHQ), 2-chlorohydroquinone (CHQ), acetic acid and oxalic acid slightly different with theoretical molecular weight (± 5) which may attributed to that compound have the secondary characteristic masses (m/z) or low concentration which was faster converted to carbon dioxide within the long time of reaction. From these data it can be suggested that the path way of 2-CP degradation mechanism using ZnO and doped ZnO NP as shown in Figure 5.26. After the catalyst absorb the photon from solar light, high reactive of radicals of $\cdot\text{OH}$ and $\cdot\text{O}_2$ were generated. The $\cdot\text{OH}$ radical attacks the ortho-position and remove Cl group and replace by $\cdot\text{OH}$ to produce the catechol ($m/z=111$). The phenol ($m/z=94$) was formed by loss of OH group from catechol (mechanism I). The hydroxyhydroquinone (HHQ) was detected by GC-MS ($m/z=127$) produced by the attack of two position of ortho and para of 2-CP. In ortho-position, removal of Cl group by electron on condition band (e^- CB) and para-position attacks by $\cdot\text{OH}$ radical. By the loss of OH group from hydroxyhydroquinone, the catechol ($m/z=111$) and phenol ($m/z=94$) were generated (mechanism II). The 2-chlorohydroquinone (CHQ) ($m/z=141$) as the main compound of 2-CP fragmentation by attacks of the $\cdot\text{OH}$ para-position. The sequence of reactions occurs forming the hydroxyhydroquinone (HHQ) by attack of the electron of Cl group and replace by OH group. By loss of the OH group on para-position and then ortho -position, the catechol ($m/z=111$) and phenol ($m/z=94$) were produced (mechanism III). From three mechanisms, the final product was phenol ($m/z=94$) with slight change (± 5) of fragmentation characteristic masses (m/z) from hydroxyhydroquinone (HHQ), 2-chlorohydroquinone (CHQ). The $\cdot\text{OH}$ radical preferentially attacks aromatic ring of phenols because their electrophilic nature (Rao, et al. 2003). This step of attacking phenol ring leads to formation of maleic and fumaric acid ($m/z=119\pm 5$) which were converted to smaller molecular compounds. The lower molecular compounds of final fragmentation was found to be oxalic acid ($m/z=90\pm 5$) and then convert to acetic acid hydroxyl ($m/z=77\pm 5$), acetic acid ($m/z=60\pm 5$), formic acid ($m/z=46$), CO_2 ($m/z=44$), CO OH ($m/z=45$) and CH_3 ($m/z=15$) as reported in many studies (Rao et al. 2003; Bandara et al. 2001).

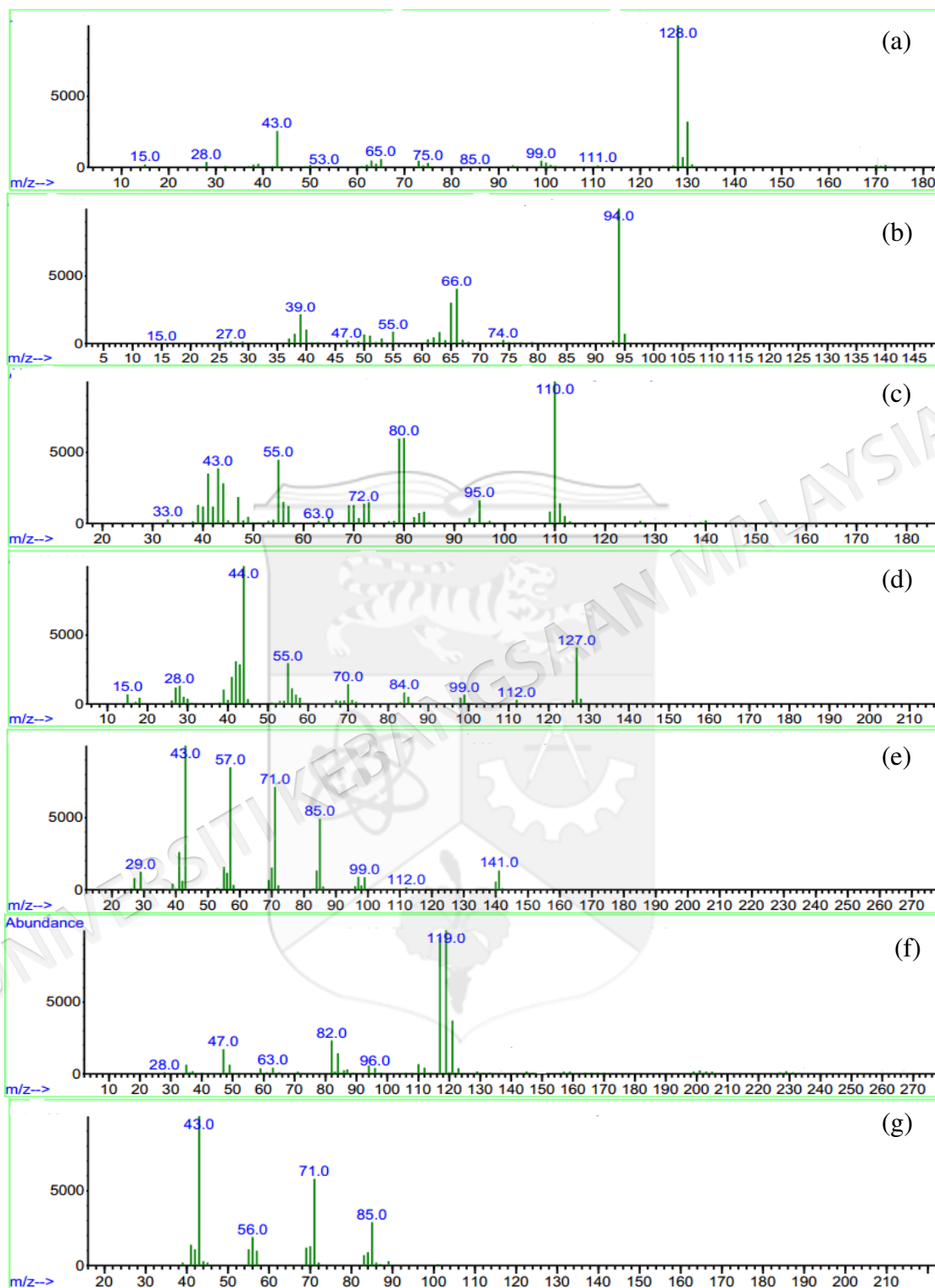


Figure 5.25 GC-MS chromatogram of degradation of 2-CP under optimum condition after 30 min irradiation time (a) 2-CP (b) phenol, (c) catechol, (d) hydroxyhydroquinone (HHQ), (e) 2-chlorohydroquinone (CHQ), (f) maleic and fumaric acid, (g) Oxalic acid.

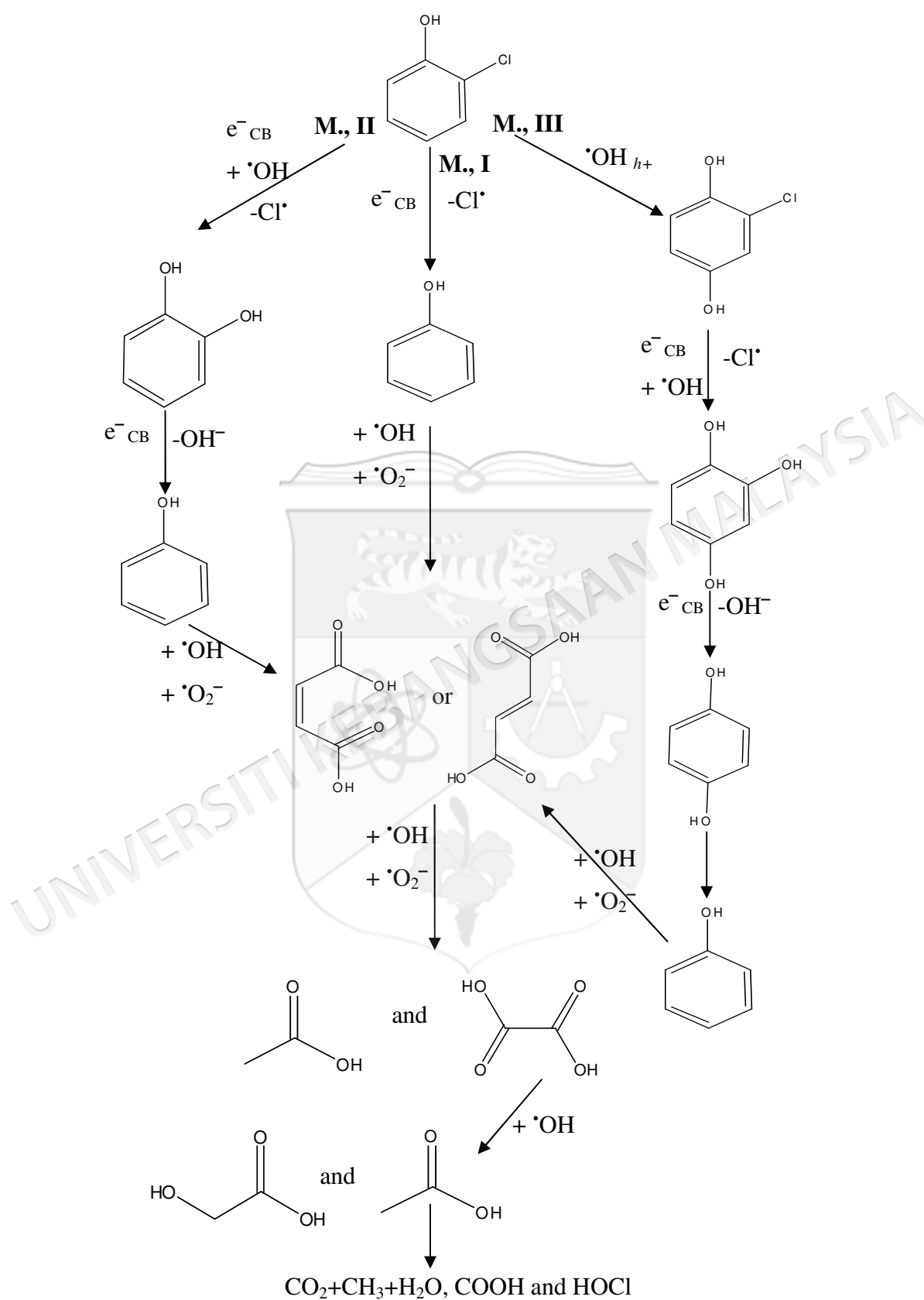


Figure 5.26 Path way fragmentation of 2-CP degradation using ZnO and doped ZnO NP under solar light.

The fragmentation of 2,4-DCP and 2,4,6-TCP shows similar mechanism with 2-CP and fragment first to 2-CP and 2,4-DCP, 2-CP respectively was reported. The characteristic masses (m/z) confirms that fragmentation of 2,4-DCP and 2,4,6-TCP to same intermediate compounds with 2-CP as shown in Figure 5.27 and Figure 5.28. The steps of 2,4-DCP and 2,4,6-TCP fragmentation mechanism using ZnO and doped ZnO under solar light were depicted in Figure 5.29 and Figure 5.30 respectively. After the fragments of 2,4-DCP and 2,4,6-TCP to 2-CP, the mechanism of intermediates formation and fragmentation to lower compounds followed the mechanism I,II and III for 2-CP as given in Figure 5.46-47. The fragmentation results of all chlorophenols showed no difference between the ZnO and doped ZnO NP which attribute to no change in structure and surface charge of ZnO before and after doping. The final products of all chlorophenols are carbon dioxide and water which non toxic compounds have been reported earlier (Ram et al. 2011; Rao et al. 2003; Bandara et al. 2001).

From GC-MS chromatogram of 2-CP, 2,4-DCP and 2,4,6-TCP, some peaks at several retention time such as 6.30, 7.43, 8.44, 9.31, 10.09 and 10.70 min were observed. The molecular structure and molecular weight of compounds were summarized in Appendix K. These compounds formed within the degradation of 2-CP, 2,4-DCP and 2,4,6-TCP after 30 min were detected. The mechanism of these compounds formation attributed to low molecules of 2-CP, 2,4-DCP and 2,4,6-TCP after attacked by super oxide radicals ($\cdot\text{O}_2^-$). Degradation of these compounds to oxalic acid and acetic acid after 60 min of irradiation time showed faster in case of 2-CP and 2,4-DCP which confirmed by HPLC in Figure 4.11 and 4.12 (a, a₁). The 2,4,6-TCP indicates bigger molecular compound was formed by two molecules which caused slow of degradation. Degradation of 2,4,6-TCP to many compounds was observed as shown in Figure 4.12(c, c₁). A 2-chloro-4-oxocyclohexanecarboxylic acid ($m/z=176\pm5$, at 10.70 min) was found from degradation of all compounds retention time of 6.30, 7.43, 8.44, 9.31 and 10.09 min. The 2-chloro-4-oxocyclohexanecarboxylic acid attacks by $\text{OH}\cdot$, $\text{O}_2^{\cdot-}$ and e^- was suggested which form the hydroquinone as intermediate compound. The fragmentation of hydroquinone to phenol and then the oxalic acid and acetic acid was followed same mechanism of degradation path way in Figure 5.26.

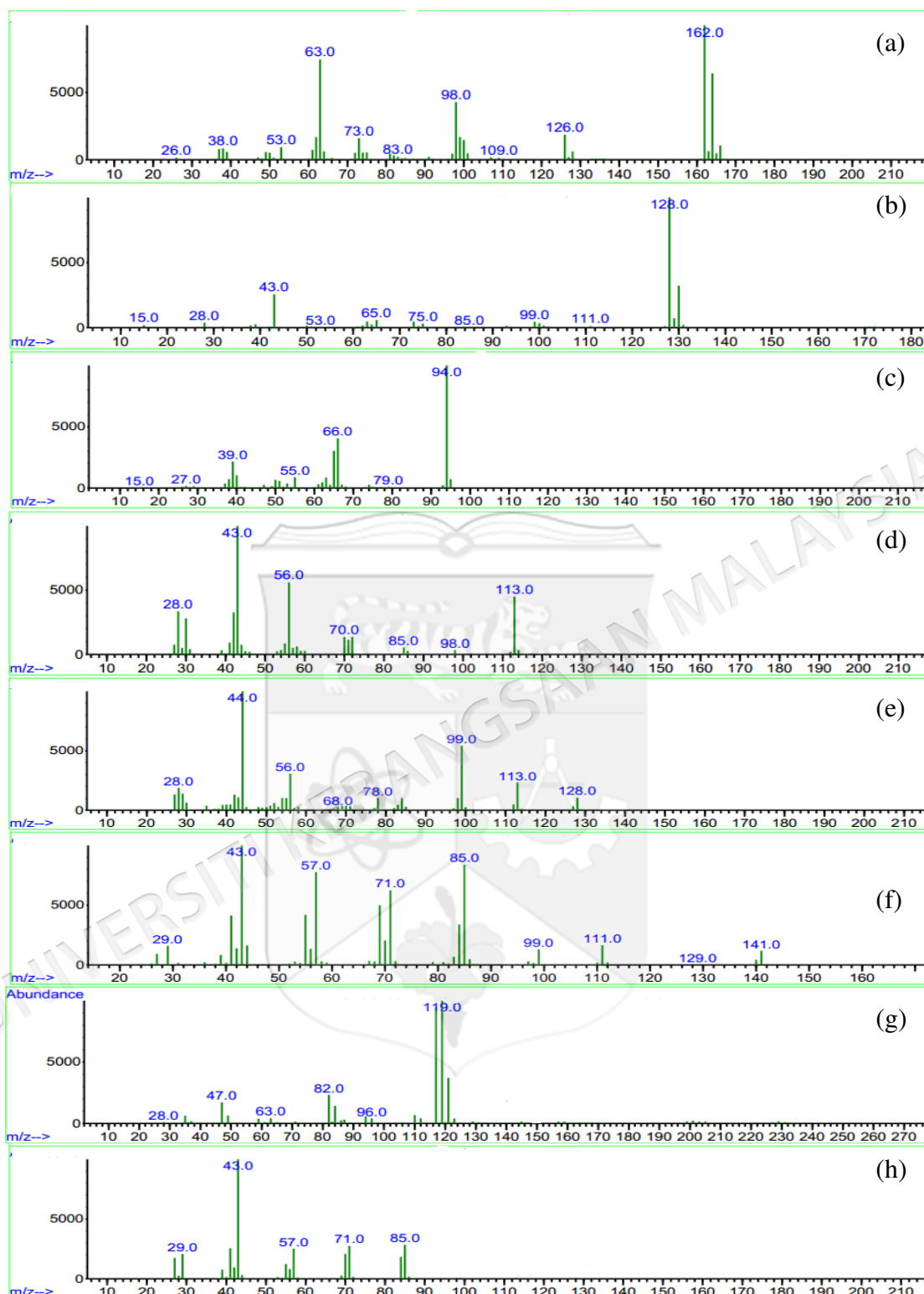


Figure 5.27 GC-MS chromatogram of degradation of 2,4-DCP under optimum condition after 30 min irradiation time (a) 2,4-DCP (b) 2-CP (c) phenol, (d) hydroquinone, (e) hydroxyhydroquinone (HHQ), (f) 2-chlorohydroquinone (CHQ), (g) maleic and fumaric acid, (h) Oxalic acid.

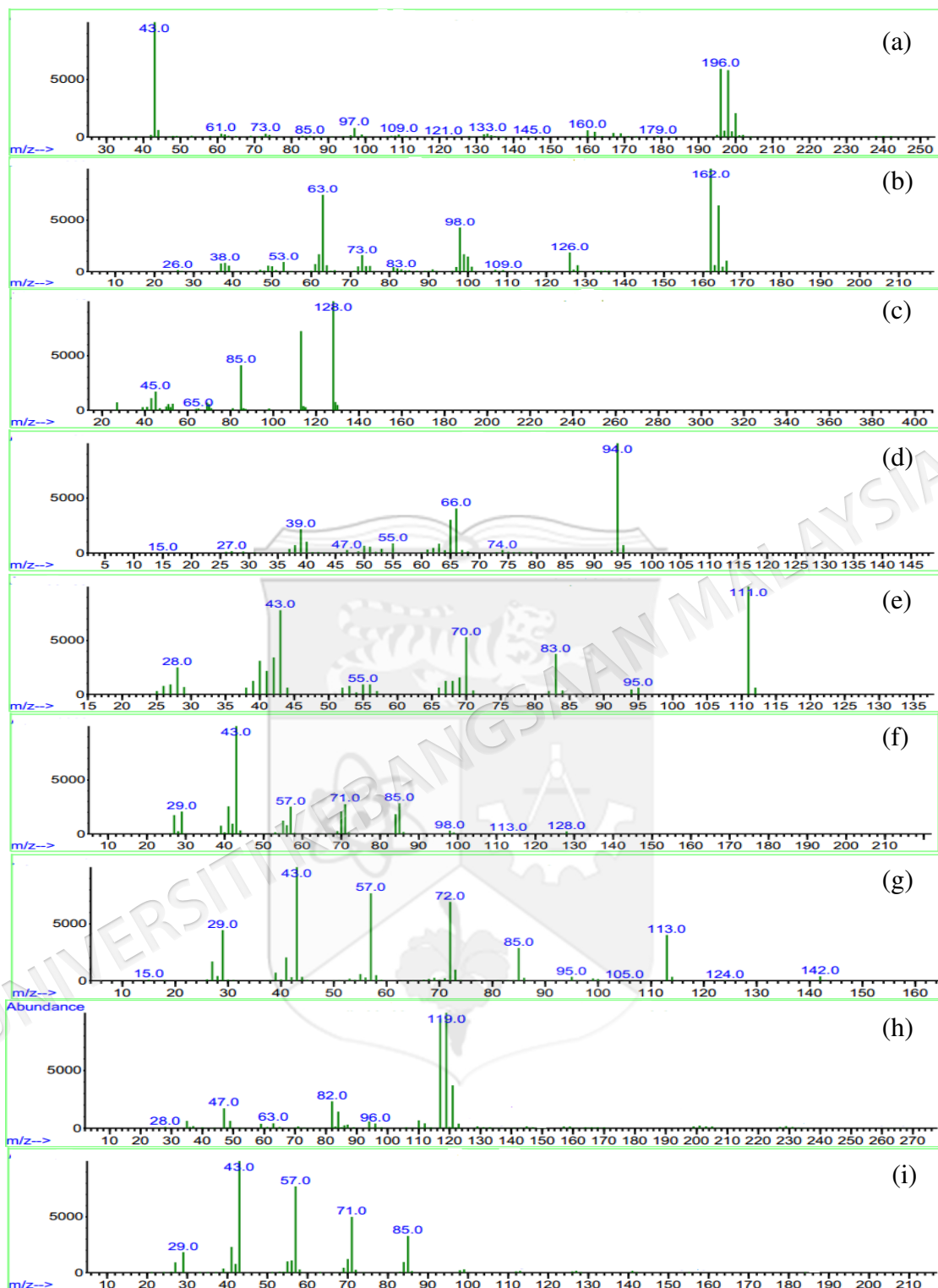


Figure 5.28 GC-MS chromatogram of degradation of 2,4,6-TCP under optimum condition after 30 min irradiation time (a) 2,4,6-TCP (b) 2,4-DCP (c) 2-CP (d) phenol, (e) catechol, (f) hydroxyhydroquinone (HHQ), (g) 2-chlorohydroquinone (CHQ), (h) maleic and fumaric acid, (i) Oxalic acid.

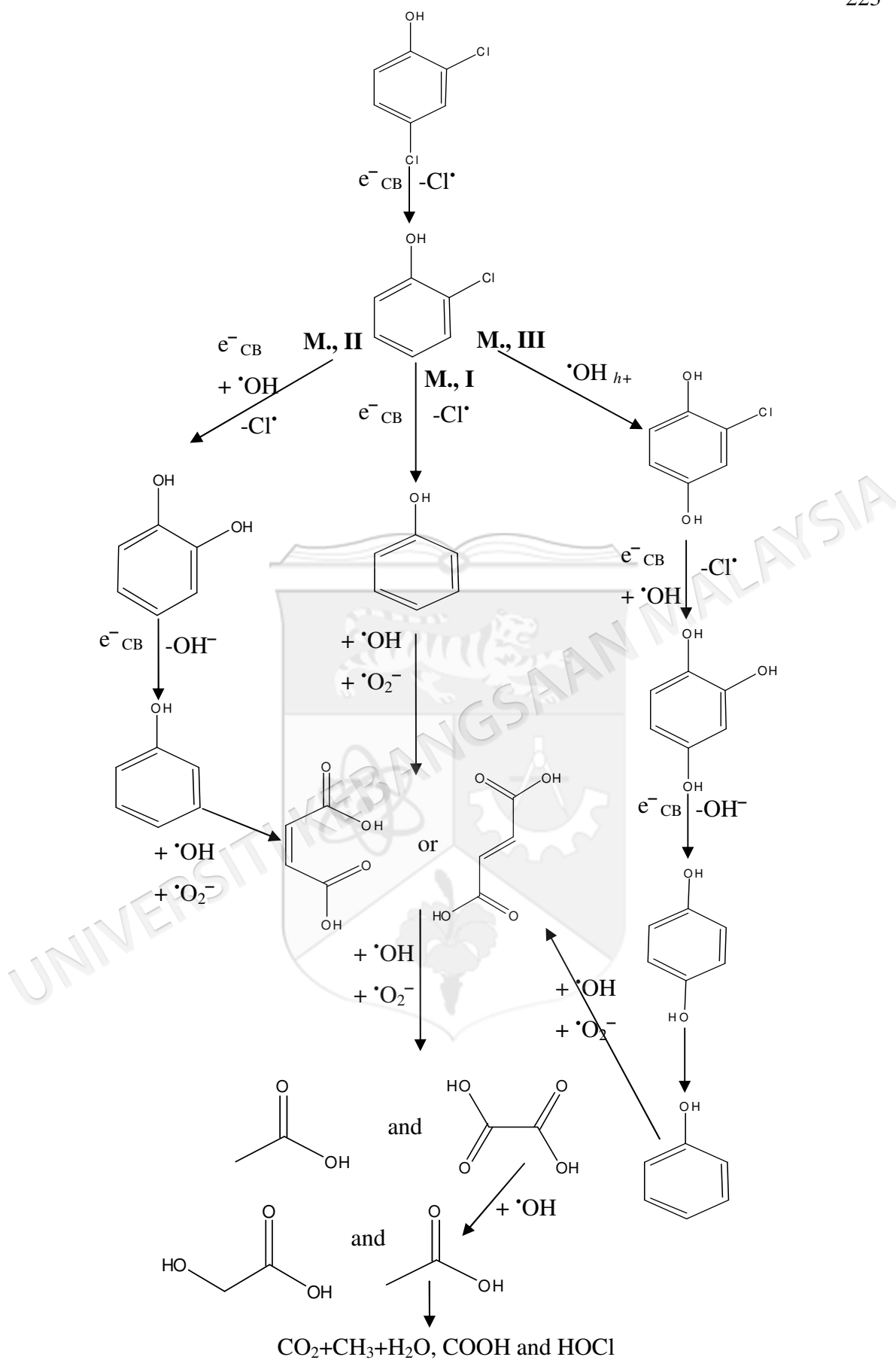


Figure 5.29 Path way fragmentation of 2,4-DCP degradation using ZnO and doped ZnO NP under solar light.

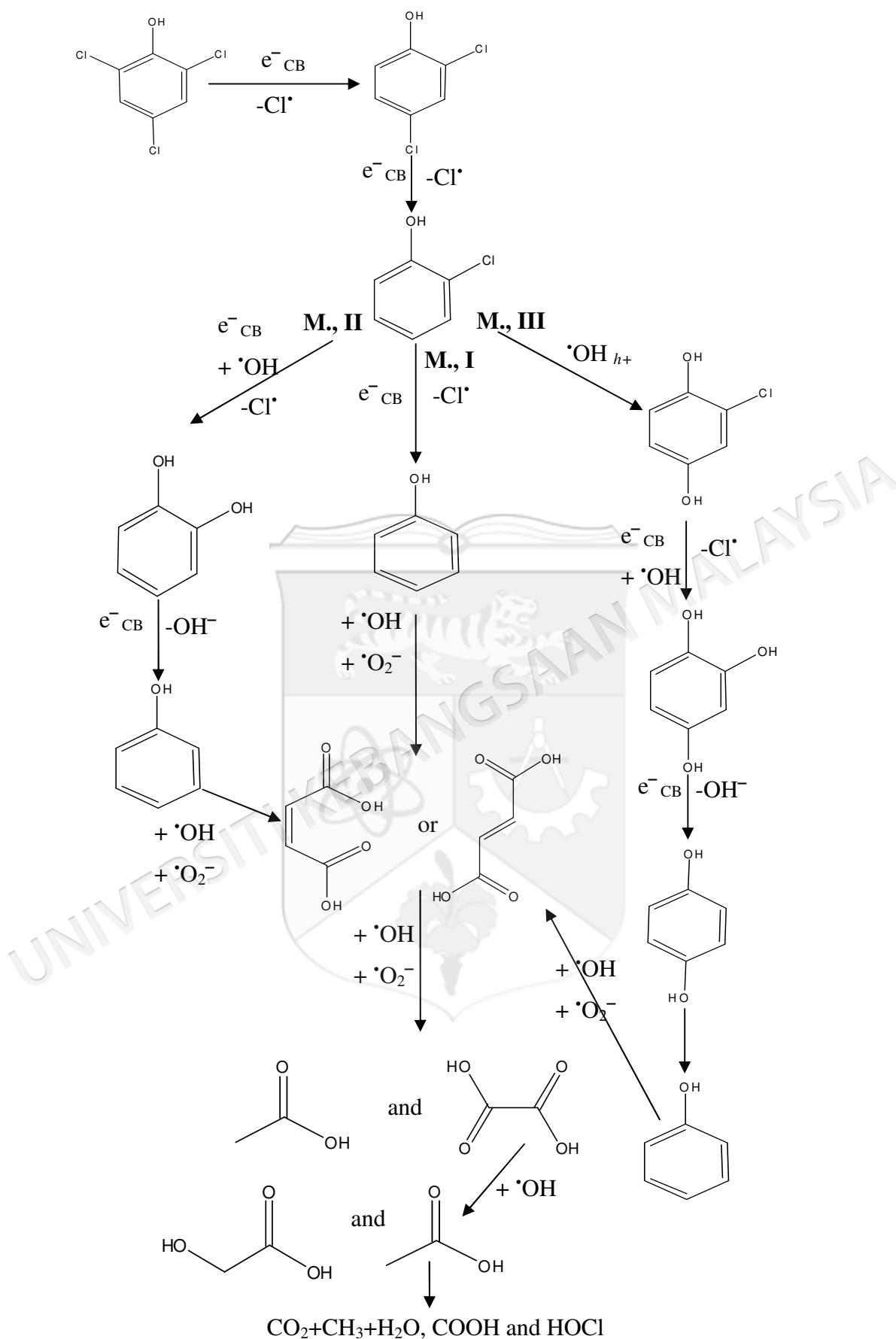


Figure 5.30 Path way fragmentation of 2,4,6-TCP degradation using ZnO and doped ZnO NP under solar light.

5.2.5 Performance of ZnO NP Activity for Degradation of Other Pollutants

To investigate the performance of ZnO NP prepared by sol gel method, some other pollutants were selected such as methyl blue, methyl orange, methyl red and lignin pink. For commercial pollutants of methyl blue, methyl orange, methyl red and lignin pink a 50 mg/l as initial concentration was used under optimum of experimental conditions of 2.0 g/l of ZnO, pH of 6.0 and sunny day of solar intensity. To determine the final concentration of methyl blue, methyl orange, methyl red and lignin pink, the UV-vis spectrophotometer was used with wavelength ($\lambda_{\max}$) of 660, 460, 430, 520 nm respectively. Figure 5.31 shows the absorbance of methyl blue, methyl orange, methyl red and lignin pink before and after degradation using the ZnO NP under direct solar light. Higher degradation efficiency of all pollutants by ZnO NP was obtained within irradiation time between the 60 to 90 min. Generally, degradation of organic dyes using the ZnO under solar light have been reported in recent year as to be the best metal oxide compared to other oxide such as TiO_2 (Han et al. 2012). These observations of ZnO due to the more absorption in UVA region and higher amount of H_2O_2 produced within the degradation process (Han et al. 2012; Shinde et al. 2011). Different optimum process parameters such as the pH, catalyst loading and source of light (UV or solar), which sometimes not suitable to compare the activity of catalyst for degradation of same pollutants. For example, almost the best of pH of color pollutants is 9.0 to 11.0 according to the survey in literature (Table 2.8) which were adjusted by adding of OH group and enhanced the degradation. The dissolution of ZnO occurs at pH around 10.0 which loss the activity for the reused as one of economical factor of the process (Han et al. 2012). To increase the activity at such high pH may more amounts used of catalyst as listed in Table 2.8. In this study pH 6.0 was applied to keep ZnO NP at higher activity by reducing the dissolution with increasing the irradiation time up to 30 min (60 to 90 min). The highest activity of ZnO NP for degradation color pollutants at pH was 5 to 7.0 as reported in the Table 2.8.

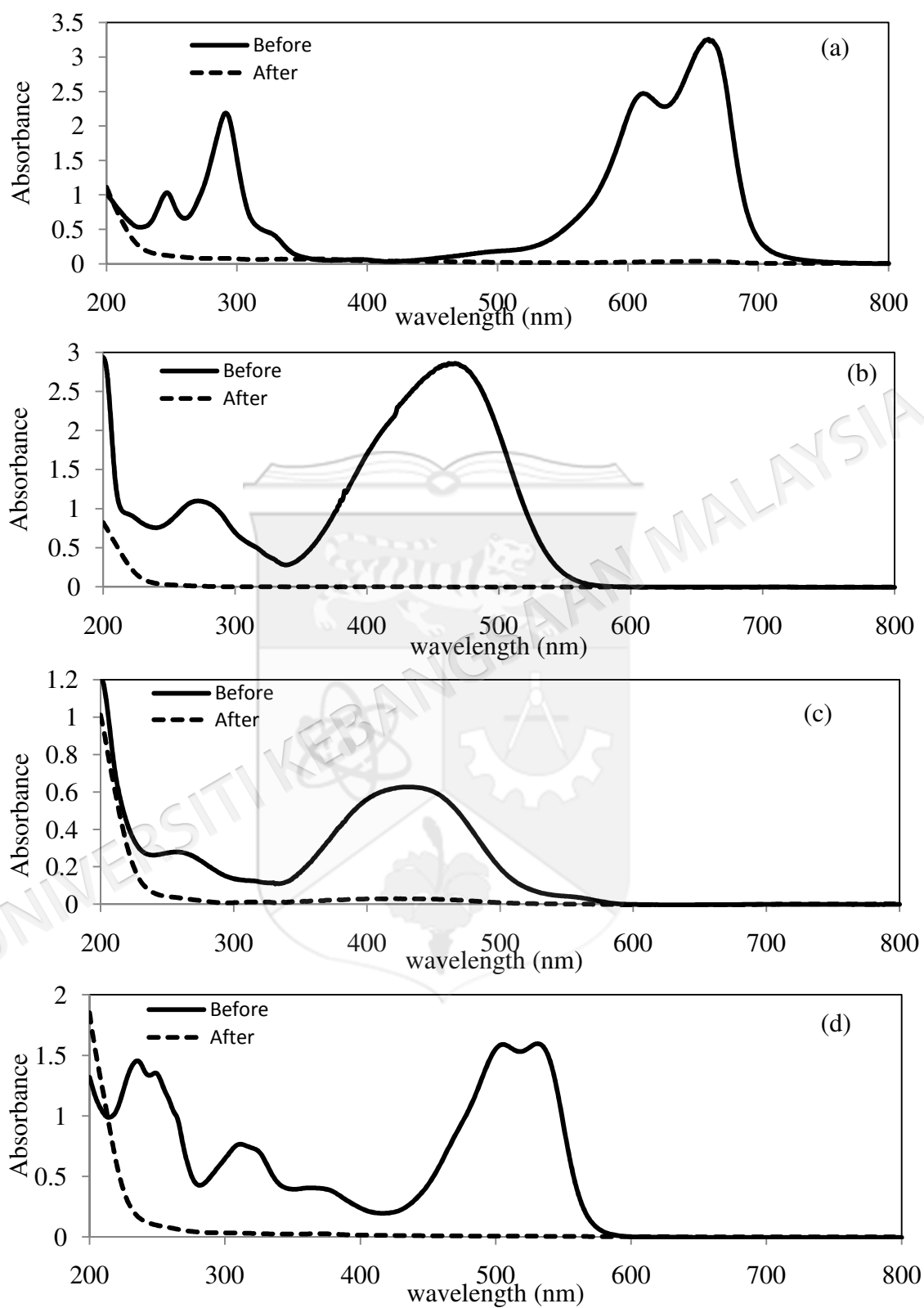


Figure 5.31 Photocatalytic degradation of pollutants using ZnO NP under solar light, (a) methyl blue, (b) methyl orange, (c) methyl red, (d) lignin

CHAPTER VI

CONCLUSION AND RECOMMENDATIONS

6.1 OVERALL CONCLUSIONS

This study has succeeded in producing smaller sized ZnO particles without any additive materials, such as capping agents or surfactants. The optimization of ZnO NP synthesized by the sol gel method using the RSM based on the D-Optimal design was investigated. The parameters (factors) that had the most effects on the morphology and size of the ZnO NP, such as the molar ratio, pH, and calcination temperature, were included in the optimization process. The factors ranging from 1 to 3, 1.0 to 5.0, and 400 to 600 °C were used for the molar ratio, pH, and calcination temperature, respectively. After running all the experiments, the good interaction between all the factors based on the D-Optimal design produced the ZnO NP with an average smaller size of 18 ± 2 and 20 ± 2 , as determined by the XRD and TEM, respectively compared to the predicted value of 22.89 nm. These results for the ZnO NP were obtained from the D-Optimal design under the optimum values of all the factors with molar ratio of 1.76, pH of 1.50 and calcination temperature at 402.2°C. In order to improve the morphology by reducing the agglomeration between the particles, a molar ratio of 2.0, pH of 2.0 ± 0.2 and calcination temperature at 402 ± 2 °C were applied. The experimental and predicted values obtained for the ZnO particle size were very close. These results showed a more economical process for the preparation of smaller sized ZnO NP by controlling the factors by RSM based on the D-Optimal design. At same time, controlling the sizes of the ZnO NP was easily indicated within the hydrolysis and condensation reaction steps of the sol gel method by controlling the process factors such as the molar ratio and pH of the media. The optimal conditions were applied for other metal oxides to make the synthesis process easier for scaling up the

production in future. All the particle sizes of the metal oxides were produced within 22 ± 4 nm, which confirmed that a higher accuracy of the model was produced from the interaction of the synthesis experiments.

The most significant factors affecting the photocatalytic degradation process were the pH of the solution, the calcination temperature and the solar intensity using the DOE based on a 2-level factorial design. Therefore, the optimization process was applied to the RSM based on the D-optimal design, which produced a more efficient model by comparing the actual with the predicted results. The optimum conditions for the degradation process between 11.00 a.m. to 12.00 p.m. showed that the highest degradation efficiency for the 2-CP model was about 90.43 %, which was in good agreement with the experimental result of 93.47 %. A higher efficiency of 97.80% was predicted by applying the highest average solar intensity of 23 between 12.00 p.m. to 1.00 p.m. A good agreement of the experimental result with 99.54% was obtained at the same experimental conditions for the pH of the solution and the calcination temperature of the catalyst. The same experimental conditions were applied for the 2,4-DCP and 2,4,6-TDCP, and the results were 97.5 and 85 %, respectively.

The optimum conditions for the highest efficiency of degradation were at pH 6.0, solar intensity for sunny days (average of 23 W/m^2), loading of catalyst at 2 g/l, calcination temperature of 400°C and initial concentration of 50 mg/l. The optimum conditions for the synthesis of ZnO were a molar ratio of 1:2 and pH of 2.0 under the same conditions of loading, solar intensity, pH of the solution and initial concentration. The degradation efficiency of the chlorophenols under optimal conditions decreased with an increase in the chloride group of phenols such as $2\text{-CP} > 2,4\text{-DCP} > 2,4,6\text{-TCP}$ for all concentrations. The results of the effects of all the process parameters (synthesis of ZnO and degradation process) on the degradation efficiency confirmed that the D-optimal design was the more appreciated design for both the synthesis of ZnO and the application process.

The doping of ZnO using Fe^{3+} , Sm^{3+} and Ti^{4+} ions showed that this was one of the best methods for enhancing the physical and optical properties for applications

under solar light. All the doped ZnO samples resulted in a higher degradation efficiency for chlorophenols compared to the undoped ZnO. The optimum doping concentration of ions were found to be 0.5 wt. % for Fe^{3+} and Sm^{3+} , and 0.25 wt. % for the Ti^{4+} ions. The higher efficiency of degradation was achieved at half the amount of the catalyst at 1 g/l compared to ZnO at 2g/l. One and a half times of the degradation efficiency was obtained at optimum loading of 1g/l compared to that of the ZnO NP. The same sequence of degradation efficiency as 2-CP > 2,4-DCP > 2,4,6-TCP were found for all concentrations of chlorophenols. The kinetic degradation as a first order reaction was found and it was the same as the kinetic reaction of undoped ZnO. To increase the efficiency of the degradation of chlorophenols, about 30 minutes of irradiation time was added to complete the degradation of lower concentrations of chlorophenols. These results showed that the degradation process by the doped ZnO samples was more economical because of the free source of energy (solar light).

Further investigations into the chlorophenol degradation process using ZnO and doped ZnO NP under optimum conditions were performed by carrying out a toxicity test using the *Escherichia coli* bacteria. The toxicity of the chlorophenol indicated by 2-CP < 2,4-DCP < 2,4,6-TCP for all the concentrations was investigated in the inhibition zone. The toxicity increased when the concentration of each chlorophenol was increased from 50 to 150 mg/l. This test indicated that the toxicity decreased as the degradation efficiency increased for both the ZnO and the doped ZnO NP. It was observed that in the small inhibition zone there was higher degradation efficiency with lower concentrations due to the presence of acetic acid as a final intermediate compound. No more Zn^{2+} ions were released during the degradation process because the ZnO and the doped ZnO NP produced only low concentrations of the ions.

The degradation of chlorophenols to nontoxic compounds such as acetic acid, carbon dioxide and lower molecular compounds using ZnO and doped ZnO NP under solar light were investigated by the HPLC and GC-MS. The mechanism of degradation from hydroxyHydroquinone, 2-chloroHydroquinone, Catechol, Hydroquinone, phenol to acetic acid, carbon dioxide and lower molecular compounds

were reported according to the GC-MS spectrum and was compared to the HPLC. This result indicated good evidence of the elimination of chlorophenol toxicity after degradation under solar light in the presence of ZnO and doped ZnO NP.

Finally, the stability of ZnO and the optimal concentration of the doped ZnO catalysts were tested for the application of chlorophenol degradation. It was shown that by repeating the degradation process for the ZnO and doped ZnO photocatalysts up to 5 times of recycling was obtained under optimal conditions. These results indicate that the higher stability of ZnO and doped ZnO synthesized by sol gel method was demonstrated within the degradation of chlorophenols. However, the degradation of other pollutants, such as dyes, from water was achieved in this study using ZnO and doped ZnO photocatalysts. All the results from the synthesis of the photocatalysts up to the applications under solar energy in this study can help to minimize the overall operational cost of the wastewater treatment industry in the future.

6.2 SUGGESTIONS FOR FUTURE WORK

Future improvements can be made to the synthesis of ZnO NP to make the applications more economical. Some of the recommendations proposed in the area of the nanoparticles and their applications:

- 1- Make a small prototype design of the continuous synthesis of metal oxide nanoparticles as a first step to scale up in the future.
- 2- Use the ZnO NP and other metal oxides for other applications such as the fabrication of membranes, solar cell, and catalyst-based biodiesel production.
- 3- A hybrid degradation of chlorophenols using ZnO and doped ZnO NP with other methods of waste treatment, such as biological methods.
- 4- Apply the ZnO and doped ZnO NP for the degradation of real waste water containing chlorophenols and colour pollutants.

REFERENCES

- Abdel Aal , A., Mahmoud , S. A. & Aboul-Gheit , A. K. 2009. Nanocrystalline ZnO thin film for photocatalytic purification of water. *Materials Science and Engineering C* 29:831–835.
- Abdollahi, Y., Abdullah, A. H., Zainal, Z. & Yusof, N. A. 2011. Synthesis and characterization of Manganese doped ZnO nanoparticles. *International Journal of Basic & Applied Sciences* 11:62-69.
- Abrishami, M. E., Kompany , A., Hosseini, S. M.& Bardar, N. G. 2012. Preparing undoped and Mn-doped ZnO nanoparticles: a comparison between sol–gel and gel-combustion methods. *Journal of Sol-Gel Science and Technology* 62:153–159.
- Ahmed, F., Kumar, S., Arshi, N., Anwar, M. S. & Koo, B. H. 2012. Morphological evolution between nanorods to nanosheets and room temperature ferromagnetism of Fe-doped ZnO nanostructures. *CrystEngComm* 14:4016-4026.
- Ahmed, S., Rasul, M.G., Brown, R. & Hashib, M.A. 2011. Influence of parameters on the heterogeneous photocatalytic degradation of pesticides and phenolic contaminants in wastewater: A short review. *Journal of Environmental Management* 92:311-330.
- Ahuja, R., Fast, L., Eriksson, O., Wills, J.M. & Johansson, B. 1998. Elastic and high pressure properties of ZnO. *Journal of Applied Physics* 83:8065-8067.
- Akyol, A., Yatmaz, H.C. & Bayramoglu, M. 2004. Photocatalytic decolorization of Remazol red RR in aqueous ZnO suspensions. *Applied Catalysis B: Environmental* 54: 19–24.
- Alam, M.Z., Muyibi, S.A. & Toramae, J. 2007. Statistical optimization of adsorption processes for removal of 2,4-dichlorophenol by activated carbon derived from oil palm empty fruit bunches. *Journal of Environmental Sciences* 19:674–677.
- Aleboyeh A., Olya M.E. & Aleboyeh, H. 2009. Oxidative treatment of azo dyes in aqueous solution by potassium permanganate. *Journal of Hazardous Materials* 162:1530-1535.
- Alhakimi, G., Gebril, S. & Studnicki, L.H. 2003. Comparative photocatalytic degradation using natural and artificial UV-light of 4-chlorophenol as a representative compound in refinery wastewater. *Journal of Photochemistry and Photobiology A: Chemistry* 157:103–109.

- Alias, S.S., Ismail, A.B. & Mohamad, A.A. 2010. Effect of pH on ZnO nanoparticle properties synthesized by sol–gel centrifugation. *Journal of Alloys and Compounds* 499: 231–237.
- Alivisatos, A.P. 1996. Semiconductor Clusters, Nanocrystals, and Quantum Dots. *Science* 271:933-937.
- Al-Janabi, K. S., Alazawi, F. N., Mohammed, M. I., Kadhum, A. H. & Mohamad, A. B. 2012. Direct Acetylation and Determination of Chlorophenols in Aqueous Samples by Gas Chromatography Coupled with an Electron-Capture Detector. *Journal of Chromatographic Science* 50:564-568.
- Aljawfi, R. N., Rahman, F. & Shukla, D.K. 2013. Effect of the annealing temperature on the structural and magnetic properties of ZnO nanoparticles. *Materials Letters* 99:18–20.
- Amma, B., Ramakrishna, K. & Pattabi, M. 2006. Comparison of various organic stabilizers as capping agents for CdS nanoparticles synthesis. *Journal of Materials Science* 18 :1109-1113.
- Anandan, S., Vinu, A., Lovely, K.S., Gokulakrishnan, N., Srinivasua, P., Mori, T., Murugesan, V., Sivamurugan, V. & Ariga, K. 2007. Photocatalytic activity of La-doped ZnO for the degradation of monocrotophos in aqueous suspension. *Journal of Molecular Catalysis A: Chemical* 266:149–157.
- Anandan, S., Vinu, A., Mori, T., Gokulakrishnan, N., Srinivasu, P., Murugesan, V. & Ariga, K. 2007(a). Photocatalytic degradation of 2,4,6-Trichlorophenol using lanthanum doped ZnO in aqueous suspension. *Catalysis Communications* 8:1377–1382.
- Anju, S.G., Yesodharan, S. & Yesodharan, E.P. 2012. Zinc oxide mediated sonophotocatalytic degradation of phenol in water. *Chemical Engineering Journal* 189–190:84–93.
- Ansaria, S.G., Wahab, R., Ansari, Z.A., Kim, Y., Khang, G., Al-Hajry, A. & Shin, H. 2009. Effect of nanostructure on the urea sensing properties of sol–gel synthesized ZnO. *Sensors and Actuators B* 137:566–573.
- Arroyo, D., Ortiz, M.C. & Sarabia, L. A. 2011. Optimization of the derivatization reaction and the solid-phase microextraction conditions using a D-optimal design and three-way calibration in the determination of non-steroidal anti-inflammatory drugs in bovine milk by gas chromatography–mass spectrometry. *Journal of Chromatography A* 1218:4487–4497.
- Arshad, M., Azama, A., Ahmed, A.S., Mollahc, S. & Naqvi, A. H. 2011. Effect of Co substitution on the structural and optical properties of ZnO nanoparticles synthesized by sol–gel route. *Journal of Alloys and Compounds* 509:8378–8381.

- Asmatulu, R., Haynes, H., Shinde, M., Lin, Y. H., Chen, Y. Y. & Ho, J. C. 2010. Magnetic Characterizations of Sol-Gel- Produced Mn-Doped ZnO. *Journal of Nanomaterials* 2010:715282-715285.
- Aydın, C., Abd El-sadek, M.S., Zheng, K., Yahia, I.S. & Yakuphanoglu, F. 2013. Synthesis, diffused reflectance and electrical properties of nanocrystalline Fe-doped ZnO via sol-gel calcination technique. *Optics & laser technology* 48:447-452.
- Ayodele, O.B., Lima, J.K.&Hameed, B.H. 2012. Degradation of phenol in photo-Fenton process by phosphoric acid modified kaolin supported ferric-oxalate catalyst: optimization and kinetic modeling. *Chemical Engineering Journal* 197:181-192.
- Azam, A., Ahmed, F., Arshi, N., Chaman, M. & Naqvi, A.H. 2010. Formation and characterization of ZnO nanopowder synthesized by sol-gel method. *Journal of Alloys and Compounds* 496:399-402.
- Babu, K. S., Reddy, R., Sujatha, C. & Reddy, K. V. 2013. Optimization of UV emission intensity of ZnO nanoparticles by changing the excitation wavelength. *Materials Letters* 99:97-100.
- Baek, S., Song, J. & Lim, S. 2007. Improvement of the optical properties of ZnO nanorods by Fe doping. *Physica B* 399:101-104.
- Bahadir, K. K. & Rauf, M.A. 2008. Application of response surface analysis to the photolytic degradation of Basic Red 2 dye. *Chemical Engineering Journal* 138:166-171.
- Bahadir, K.K. & Rauf, M.A. 2009. Determination of optimum operating conditions of carmine decoloration by UV/ H₂O₂ using response surface methodology. *Journal of Hazardous Materials* 161:281-286.
- Ban, C., Chernova, N. A. & Whittingham, M. S. 2009. Electrospun nano-vanadium pentoxide cathode. *Electrochemistry Communications* 11:522-525.
- Bandara, J., Mielczarski, J.A., Lopez, A. & Kiwi, J. 2001. 2. Sensitized degradation of chlorophenols on iron oxides induced by visible light Comparison with titanium oxide. *Applied Catalysis B: Environmental* 34:321-333.
- Baruah, S. & Dutta, J. 2009. pH-dependent growth of zinc oxide nanorods. *Journal of Crystal Growth* 311:2549-2554.
- Baruah, S., Mahmood, M. A., Myint, M. T. Z., Bora, T. & Dutta, J. 2010. Enhanced visible light photocatalysis through fast crystallization of zinc oxide nanorods. *Beilstein Journal of Nanotechnology* 1:14-20.
- Baruah, S., Pal, S. K. & Dutta, J. 2012. Nanostructured Zinc Oxide for Water Treatment, *Nanoscience & Nanotechnology-Asia* 2:90-102.

- Behnajady, M.A., Modirshahla, N. & Hamzavi, R. 2006. Kinetic study on photocatalytic degradation of C.I. Acid Yellow 23 by ZnO photocatalyst. *Journal of Hazardous Materials* 133:226–232.
- Behrends, A., Bakin, A. & Waag, A. 2009. Investigation of ZnO nanopillars fabrication in a new Thomas Swan close coupled showerhead MOCVD reactor. *Microelectronics Journal* 40:280–282.
- Beydoun, D., Amal, R., Low, G. & McEvoy, S. 1999. Role of Nanoparticles in Photocatalysis. *Journal of Nanoparticle Research* 1: 439-458.
- Bosco, M. & Larrechi, M.S. 2008. Rapid and quantitative evaluation of the effect of process variables on the kinetics of photocatalytic degradation of phenol using experimental design techniques and parallel factor (PARAFAC) analysis. *Analytical and Bioanalytical Chemistry* 390:1203–1207.
- Bosman, M., Keast, V. J., Watanabe, M., Maarroof, A. I. & Cortie, M.B. 2007. Mapping surface plasmons at the nanometre scale with an electron beam. *Nanotechnology* 18: 165505.
- Box, G. & Draper, N. 1987. *Wiley Series in Probability and Mathematical Statistics: Applied Probability and Statistics*. New Jersey: John Wiley & Sons Inc.
- Box, G. E. P. & Wilson K. B. 1951. On the experimental attainment of optimum conditions. *Journal of the Royal Statistical Society: Series B* 13:1–45.
- Box, G.E.P. & Behnken, D.W. 1960. Some New Three Level Designs for the Study of Quantitative Variables. *Technometrics* 2:455-475.
- Box, J G.E.P., Hunter, S. & Hunter, W.G. 2005. *Statistics for Experimenters: Design, Innovation, and Discovery*, second ed. New Jersey: Wiley Interscience.
- Brandmaier, S., Sahlin, U., Tetko, I. V. & Öberg, T. 2012. PLS-Optimal: A Stepwise D-Optimal Design Based on Latent Variables. *Journal of Chemical Information and Modeling* 52:975–983.
- Braslavsky, S.E. 2007. Glossary of terms used in photochemistry 3rd Edition (IUPAC Recommendations 2006). *Pure Applied Chemistry* 79:293-465.
- Brinker, C. J. & Scherer, G. W. 1990. *Sol-gel Science: The Physics and Chemistry of Sol-gel Processing*. USA: Academic press, Inc.
- Brunauer, S., Emmett, P. H. & Teller E. 1938. Adsorption of gases in multimolecular layers. *Journal of the American Chemical Society* 60:309-319.
- Buesser, B. & Pratsinis, S.E. 2010. Design of aerosol particle coating: texture, thickness and efficiency. *Chemical Engineering Science* 65:5471-5481.

- Carp, O., Huisman, C.L. & Reller, A. 2004. Photoinduced reactivity of titanium dioxide, *Progress in Solid State Chemistry* 32:33-177.
- Carreon, M.A. & Gulians, V.V. 2005. Ordered meso- and macroporous binary and mixed metal oxides. *European Journal of Inorganic Chemistry* 1:27-43.
- Chandrasekaran, P., Viruthagiri, G. & Srinivasan, N. 2012. The effect of various capping agents on the surface modifications of sol-gel synthesised ZnO nanoparticles. *Journal of Alloys and Compounds* 540:89-93.
- Chen, D. & Ray, A.K. 1999. Photocatalytic kinetics of phenol and its derivatives over UV irradiated TiO₂. *Applied Catalysis B: Environmental* 23:143-157.
- Chen, K.J., Fang, T.H., Hung, F.Y., Ji, L.W., Chang, S.J., Young, S.J. & Hsiao, Y.J., 2008. The crystallization and physical properties of Al-doped ZnO nanoparticles. *Applied Surface Science* 254:5791-5795.
- Chen, S., Zhao, W., Liu, W. & Zhang, S. 2009. Preparation, characterization and activity evaluation of p-n junction photocatalyst p-NiO/n-ZnO. *Journal of Sol-Gel Science and Technology* 50:387-396.
- Chen, X. & Mao, S. 2007. Titanium dioxide nanomaterials: Synthesis, properties, modifications, and applications. *Chemical Reviews* 107:2891-2959.
- Chen, X. Y., W. Luo, Q., Liu, Y. S. & Liu, G. K. 2007. Recent progress on spectroscopy of lanthanide ions incorporated in semiconductor nanocrystals. *Journal Rare Earths* 25:515-525.
- Chen, Z., Tang, Y., Zhang, L. & L. Lu. 2006. Electrodeposited nanoporous ZnO films exhibiting enhanced performance in dye-sensitized solar cells. *Electrochimica Acta* 51:5870-5875.
- Chieng, B. W. & Loo, Y. Y. 2012. Synthesis of ZnO nanoparticles by modified polyol method. *Materials Letters* 73:78-82.
- Chiou, W. T., Wu, W. Y. & Ting, J. M. 2003. Growth of single crystal ZnO nanowires using sputter deposition. *Diamond and Related Materials* 12:1841-1844.
- Coey, J. M. D., Venkatesan, M. & Fitzgerald, C. B. 2005. Donor impurity band exchange in dilute ferromagnetic oxides. *Nature Mater* 4:173-179.
- Cullity, B. & Stock, S.R. 2001. *Elements of X-ray Diffraction*, third edition, Prentice Hall, UAS.
- Cushing, B.L., Kolesnichenko, V.L. & Connor, C.J.O. 2004. Recent advances in the liquid-phase syntheses of inorganic nanoparticles. *Chemical Reviews* 104:3893-946.

- Czaplicka, M. 2006. Photo-degradation of chlorophenols in the aqueous solution. *Journal of Hazardous Materials* 134:45–59.
- Dakhlaoui, A., Jendoubi, M., Smiri, L.S., Kanaev, A. & Jouini, N. 2009. Synthesis, characterization and optical properties of ZnO nanoparticles with controlled size and morphology. *Journal of Crystal Growth* 311:3989–3996.
- Daneshvar, N., Aber, S., Dorraji, M.S.S., Khataee, A.R. & Rasoulifard, M.H. 2007. Photocatalytic degradation of the insecticide diazinon in the presence of prepared nanocrystalline ZnO powders under irradiation of UV-C light. *Separation and Purification Technology* 58:91-98.
- Daniel, M.C. & Astruc, D. 2003. Gold nanoparticles: assembly, supramolecular chemistry, quantum-size-related properties, and applications toward biology, catalysis, and nanotechnology. *Chemical Reviews* 104:293-346.
- Debernardi, A. & Fanciulli, M. 2007. The magnetic interaction of Fe doped ZnO with intrinsic defects: A first principles study. *Physica B* 401–402:451-453.
- Demeestere, K., Dewulf J. & Langenhove, H. 2007. Heterogeneous Photocatalysis as an Advanced Oxidation Process for the Abatement of Chlorinated, Monocyclic Aromatic and Sulfurous Volatile Organic Compounds in Air: State of the Art. *Critical Reviews in Environmental Science and Technology* 37:489-538.
- Devillers, J. & Chambon, P. 1986. Acute toxicity and QSAR of chlorophenols on *Daphnia magna*. *Bulletin of Environmental Contamination and Toxicology* 37:599–605.
- Devipriya, S.P. & Yesodharan, S. 2010. Photocatalytic degradation of phenol in water using TiO₂ and ZnO. *Journal of Environmental Biology* 31:247-249.
- Diao, Y.L., Walawender, W.P., Sorensen, C.M., Klabunde, K.J. & Ricker, T. 2001. Hydrolysis of magnesium methoxide: Effects of toluene on gel structure and gel chemistry. *Chemistry of Materials* 14: 362-368.
- Diaz Cano, A.I., El Filali, B., Torchynska, T.V. & Casas Espinola, J.L. 2013. Structure and emission transformations in ZnO nanosheets at thermal annealing. *Journal of Physics and Chemistry of Solids* 74:431–435.
- Díez, A. R., Sarabia, L.A. & Ortiz, M.C. 2010. Optimization of a solid-phase extraction procedure in the fluorimetric determination of sulfonamides in milk using the second-order advantage of PARAFAC and D-optimal design. *Analytical and Bioanalytical Chemistry* 396:923-935.
- Díez, R., Sarabia, L. & Ortiz, M.C. 2007. Optimization of analytical conditions and validation of a fluorescence method for the determination of sulfadiazine in milk. *Analytical and Bioanalytical Chemistry* 388:957-968.

- Dios, M., Barroso, F., Tojo, C., Blanco, M.C. & L'opez-Quintel, M.A. 2005. Effects of the reaction rate on the size control of nanoparticlessynthesized in microemulsions, *Colloids and Surfaces A* 270:83–87.
- Dutta1, S. & Ganguly, B. N. 2012. Characterization of ZnO nanoparticles grown in presence of Folic acid template. *Journal of Nanobiotechnology* 10: 29-39.
- El-Bahy, Z.M., Ismail, A.A. & Mohamed, R.M. 2009. Enhancement of titania by doping rare earth for photodegradation of organic dye (Direct Blue). *Journal of Hazardous Materials* 166:138-14.
- El-Ghoul, J., Barthou, C. & El Mir, L. 2012. Synthesis, structural and optical properties of nanocrystalline vanadium doped zinc oxide aerogel. *Physica E* 44:1910–1915.
- Elias, J., Tena-Zaera, R. & Lévy-Clément, C. 2008. Electrochemical deposition of ZnO nanowire arrays with tailored dimensions. *Journal of Electroanalytical Chemistry* 621:171–177.
- El-Kemary, M., H. & El-Mehasseb, I. 2010. Photocatalytic degradation of ciprofloxacin drug in water using ZnO nanoparticles. *Journal of Luminescence* 130:2327–2331.
- Elmolla, E. S. & Chaudhuri, M. 2010. Degradation of amoxicillin, ampicillin and cloxacillin antibiotics in aqueous solution by the UV/ZnO photocatalytic process. *Journal of Hazardous Materials* 173:445–449.
- Eriksson, J., Khranovskyy, V., Söderlind, F., Käll, P., Yakimova, R. & Spetz, A. 2009. ZnO nanoparticles or ZnO films: A comparison of the gas sensing capabilities. *Sensors and Actuators B: Chemical* 137:94–102.
- Eriksson, L., Johansson, E., Kettaneh-Wold, N., WikstrÄom, C. & Wold, S. 2000. *Design of Experiments: Principles and Applications*, Learnways AB, Umea.
- Evgenidou, E., Fytianos, K. & Poullos, I. 2005. Semiconductor-sensitized photodegradation of dichlorvos in water using TiO₂ and ZnO as catalysts. *Applied Catalysis B: Environmental* 59:81–89.
- Fabbri, D., Prevot, A. B. & Pramauro, E. 2006. Effect of surfactant microstructures on photocatalytic degradation of phenol and chlorophenols. *Applied Catalysis B: Environmental* 62: 21–27.
- Fenoll, J., Hellin, P., Flores, P., MartInez, C. M. & Navarro, S. 2013. Degradation intermediates and reaction pathway of carbofuran in leaching water using TiO₂ and ZnO as photocatalyst under natural sunlight. *Journal of Photochemistry and Photobiology A: Chemistry* 251:33– 40.

- Fenoll, J., Hellin, P., MartInez, C. M., Flores, P. & Navarro, S. 2012a. Semiconductor oxides-sensitized photodegradation of fenamiphos in leaching water under natural sunlight. *Applied Catalysis B: Environmental* 115–116:31– 37.
- Fenoll, J., Hellin, P., Martinez, C.M., Flores, P. & Navarro, S. 2012b. Semiconductor-sensitized photodegradation of s-triazine and chloroacetanilide herbicides in leaching water using TiO₂ and ZnO as catalyst under natural sunlight. *Journal of Photochemistry and Photobiology A: Chemistry* n238:81– 87.
- Fenoll, J., Ruiz, E., Hellin, P., Flores, P. & Navarro, S. 2011. Heterogeneous photocatalytic oxidation of cyprodinil and fludioxonil in leaching water under solar irradiation. *Chemosphere* 85:1262–1268.
- Fernandes, D. M., Silva, R., W. Hechenleitner, A. A., Radovanovic, E., Melo, M. A. C. & Pineda, E. A. G. 2009. Synthesis and characterization of ZnO, CuO and a mixed Zn and Cu oxide. *Materials Chemistry and Physics* 115:110–115.
- Fu, H., Li, H., Jie, & Zhang, C. 2007. The O₂-dependent growth of ZnO nanowires and their photoluminescence properties. *Ceramics International* 33:1119–1123.
- Fujishima, A., Zhang, X. & Tryk, D.A. 2007. Heterogeneous photocatalysis: from water photolysis to applications in environmental cleanup. *International Journal of Hydrogen Energy* 32: 2664–2672.
- Gaya, U. I. & Abdullah, A. H. 2008. Heterogeneous photocatalytic degradation of organic contaminants over titanium dioxide: A review of fundamentals, progress and problems. *Journal of Photochemistry and Photobiology C* 9:1–12.
- Gaya, U. I., Abdullah, A. H., Hussein, M.Z. & Zainal, Z. 2009. Photocatalytic treatment of 4-chlorophenol in aqueous ZnO suspensions: intermediates, influence of dosage and inorganic anions. *Journal of Hazardous Materials* 168:57–63.
- Gaya, U. I., Abdullah, A. H., Hussein, M.Z. & Zainal, Z. 2010 a. Photocatalytic removal of 2,4,6-trichlorophenol from water exploiting commercial ZnO powder. *Desalination* 263:176–182.
- Gaya, U. I., Abdullah, A. H., Hussein, M.Z. & Zainal, Z. 2010b. Photocatalytic Degradation of 2,4-dichlorophenol in Irradiated Aqueous ZnO Suspension. *International Journal of Chemistry* 2:180–193.
- Ghoshal, T., Kar, S. & Chaudhuri, S. 2006. Synthesis and optical properties of nanometer to micrometer wide hexagonal cones and columns of ZnO. *Journal of Crystal Growth* 293:438–446.

- Gilmour, S.G. 2006. Response surface designs for experiments in bioprocessing. *Biometrics* 62:323-331.
- Gleiter, H. 2000. Nanostructured Materials: Basic Concepts and Microstructure. *Acta Materialia* 48:1-29.
- Goswami, N. & Sharma, D. K. 2010. Structural and Optical Properties of Unannealed and Annealed ZnO Nanoparticles Prepared by a Chemical Precipitation Technique. *Physica E* 42:1675-1682.
- Grcic I., Vujević D. & Koprivanac N. 2010. The use of D-optimal design to model the effects of process parameters on mineralization and discoloration kinetics of Fenton-type oxidation, *Chemical Engineering Journal* 157:408–419.
- Gröhn, A.J., Buesser, B., Jokiniemi, J. & Pratsinis, S.E. 2011. Design of turbulent flame aerosol reactors by mixing-limited fluid dynamics. *Industrial and Engineering Chemistry Research* 50:3159-68.
- Gruendling, T., Guilhaus, M. & Barner-Kowollik, C. 2009. Design of Experiment (DOE) as a Tool for the Optimization of Source Conditions in SEC-ESI-MS of Functional Synthetic Polymers Synthesized via ATRP. *Macromolecular Rapid Communications* 30:589-597.
- Grzechulska, J. & Morawski, A.W. 2002. Photocatalytic decomposition of azo-dye acid black 1 in water over modified titanium dioxide. *Applied Catalysis B: Environmental*, 36:45-51.
- Hammad, T.M., Salem, J.K. & Harrison, R.G. 2009. Binding Agent Affect on the structural and optical properties of ZnO Nanoparticles. *Reviews on Advanced Materials Science* 22:74-80.
- Han, J., Liu, Y., Singhal, N., Wang, L. & Gao, W. 2012. Comparative photocatalytic degradation of estrone in water by ZnO and TiO₂ under artificial UVA and solar irradiation. *Chemical Engineering Journal* 213:150–162.
- Hariharan. C. 2006. Photocatalytic degradation of organic contaminants in water by ZnO nanoparticles: Revisited. *Applied Catalysis A: General* 304:55–61.
- Hasan, D.B., Abdul Aziz, A.R. & Daud, W.M. 2012. Using D-optimal experimental design to optimise remazol black B mineralisation by Fenton-like peroxidation. *Environmental Technology* 33:1111-1121.
- Hassan, M. M., Ahmed, A. S., Chaman, M., Khan, W., Naqvi, A.H. & Azam, A. 2012. Structural and frequency dependent dielectric properties of Fe³⁺ doped ZnO nanoparticles. *Materials Research Bulletin* 47:3952–3958.
- Hassan, M. M., Ahmed, A. S., Chaman, M., Khan, W., Naqvi, A.H. & Azam, A. 2012. Structural and frequency dependent dielectric properties of Fe³⁺ doped ZnO nanoparticles. *Materials Research Bulletin* 47:3952–3958.

- Hassan, M. M., Khan, W., Azama, A. & Naqvi, A.H. 2014. Effect of size reduction on structural and optical properties of ZnO matrix due to successive doping of Fe ions. *Journal of Luminescence* 145:160–166.
- Hayat, K., Gondal, M.A., Khaled, M.M., Ahmed, S. & Shemsi, A. M. 2011. nano-ZnO synthesis by modified sol gel method and its application in heterogeneous photocatalytic removal of phenol from water. *Applied catalysis A: general* 393:122-129.
- Herrmann, J., Duchamp, C., Karkmaz, M., Hoai, B., Lachheb, H., Puzenat, E. & Guillard, C. 2007. Environmental green chemistry as defined by photocatalysis. *Journal of Hazardous Material* 146: 624-629.
- Herrmann, J.M. 2005. Heterogeneous photocatalysis: state of the art and present applications. *Topics in Catalysis* 34:49-65.
- Hilal, S.W., Bredow, T. & Aliwi, S. M. 2008. Computational modeling of the adsorption and photodegradation of 4-chlorophenol on anatase TiO₂ particles. *Journal of Molecular Structure: THEOCHEM* 863:84–90.
- Hoffmann, M. R., Martin, S. T., Choi, W. & Bahnemann, D. W. 1995. Environmental applications of semiconductor photocatalysis. *Chemical Reviews* 95:69-96.
- Hong, J. I., Bae, J., Wang, Z. L. & Snyder, R. L. 2009. Room temperature, texture-controlled growth of ZnO thin films and their application for growing aligned ZnO nanowire arrays. *Nanotechnology* 20:085609-085614.
- Hou, Y., Yang, M., Pang, G.S. & Feng, S.H. 2008. ZnO microrods with etched surface prepared by two-step hydrothermal reaction. *Journal of Materials Science* 43:2149-2152.
- Hu, L., Song, H., Pan, G., Yan, B., Qin, R., Dai, Q., Fan, L., Li, S. & Bai, X. 2007. Photoluminescence properties of samarium-doped TiO₂ semiconductor nanocrystalline powders. *Journal of Luminescence* 127:371-376.
- Hu, X., Li, G. & Yu, J. C. 2010. Design, fabrication, and modification of nanostructured semiconductor materials for environmental and energy applications. *Langmuir* 26:3031-3039.
- Hu, Z., Herrera Santos, J.F., Oskam, G. & Searson, P. C. 2005. Influence of the reactant concentrations on the synthesis of ZnO Nanoparticles. *Journal of Colloid and Interface Science* 288:313–316.
- Huang, L., Wei-Lan X. & Zuo-Xiang, Z. 2011. The Solubility of ammonia in ethanol between 277.35 K and 328.15 K. *Fluid Phase Equilib* 303:80–84.

- Huang, W., Fang, G. & Wang, C. 2005. A nanometer-ZnO catalyst to enhance the ozonation of 2,4,6-trichlorophenol in water. *Colloids and Surfaces A*: 260:45–51.
- Hung, C.H. & Whang, W.T. 2003. A novel low-temperature growth and characterization of single crystal ZnO nanorods. *Materials Chemistry and Physics* 82:705–710.
- Isley S.L. & Penn R.L. 2008. Titanium dioxide nanoparticles: Effect of sol-gel pH on phase composition, particle size, and particle growth mechanism. *The Journal of Physical Chemistry C* 112:4469–4474.
- Ismail, A.A., El-Midany, A., Abdel-Aal, E.A. & El-Shall, H. 2005. Application of statistical design to optimize the preparation of ZnO nanoparticles via hydrothermal technique. *Materials Letters* 59:1924–1928.
- Jafarzadeh, N. K., Sharifnia, S., Hosseini, S. N., & Rahimpour, F. 2011. Statistical optimization of process conditions for photocatalytic degradation of phenol with immobilization of nano TiO₂ on perlite granules. *Korean Journal of Chemical Engineering* 28: 531–538.
- Janackovic, D., Jokanovic, V., Kostic-Gvozdenovic, L. & Uskokovic, D. 1998. Synthesis of Mullite Nanostructured Spherical Powder by the Ultrasonic Spray Pyrolysis. *Nanostructured Materials* 10:333–339.
- Jeong, C., Kim, H., Chang, D. & Kamisako, K. 2008. Effect on Al₂O₃ Doping Concentration of RF Magnetron Sputtered ZnO:Al Films for Solar Cell Applications. *Japanese Journal of Applied Physics* 47:5656–5658.
- Jin, W., Lee, I., Kompch, A., Dörfler, U. & Winterer, M. 2007. Chemical vapor synthesis and characterization of chromium doped zinc oxide nanoparticles. *Journal of the European Ceramic Society* 27:4333–4337.
- Jiye, A., Trygg, J., Gullberg, J., Johansson, A.I., Jonsson, P., Antti, H., Marklund, S.L. & Moritz, T. 2005. Extraction and GC/MS analysis of the human blood plasma metabolome. *Analytical Chemistry*, 77:8086–8094.
- Jones, A.P. & Watts, R.J. 1997. Dry phase dioxide-mediated photocatalysis: basis for in situ surface destruction of hazardous chemicals. *Journal of Environmental Engineering* 123:974–981.
- Kang, Y., Choi, C., Kim, Y. & Kim, J. 2009. Influence of seed layers on the vertical growth of ZnO nanowires. *Materials Letters* 63:679–682.
- Kansal, S. K., Singh, M. & Sud, D. 2009. Optimization of Process Parameters for the Photocatalytic Degradation of 2,4-Dichlorophenol in Aqueous Solutions. *International Journal of Chemical Reactor Engineering* 7: 1–22.

- Kansal, S.K., Singh, M. & Sud, D. 2007a. Optimization of photocatalytic process parameters for the degradation of 2,4,6-trichlorophenol in aqueous solutions. *Chemical Engineering Communications* 194:787–802.
- Kansal, S.K., Singh, M. & Sud, D. 2007b. Parametric Optimization of Photocatalytic Degradation of Catechol in Aqueous Solutions by Response Surface Methodology. *Indian Journal of Chemical Technology* 14:145-153.
- Kant, S. & Kumar, A. 2012. A comparative analysis of structural, optical and photocatalytic of ZnO and Ni doped ZnO nanospheres prepared by sol-gel. *Advanced Material Letter* 3:350-354.
- Karacan, F., Ozden, U. & Karacan, S. 2007. Optimization of manufacturing conditions for activated carbon from Turkish lignite by chemical activation using response surface methodology. *Applied Thermal Engineering* 27:1212-1218.
- Karmakar, D., Mandal, S.K., Kadam, R.M., Paulose P.L., Rajarajan A.K., Nath T.K., Das A.K., Dasgupta I. & Das G.P. 2007. Ferromagnetism in Fe-doped ZnO nanocrystals: Experiment and theory. *Physical Review B* 75:144404-144418.
- Karunakaran, C. & Dhanalakshmi, R. 2008. Semiconductor-catalyzed degradation of phenols with sunlight. *Solar Energy Materials & Solar Cells* 92:1315– 1321.
- Kaur, R., Singh, A.V., Sehrawat, K., Mehra, N.C. & Mehra, R.M. 2006. Sol-gel derived yttrium doped ZnO nanostructures. *Journal of Non-Crystalline Solids* 352: 2565–2568.
- Kayalvizhi, N. & Gunasekaran, P. 2010. Purification and Characterization of a Novel Broad-spectrum Bacteriocin from *Bacillus licheniformis* MKU3. *Biotechnology and Bioprocess Engineering*, 15: 365-370.
- Keith, L.H. & Telliard, W.A. 1979. ES & T special report priority pollutants: I-a perspective view. *Environmental Science & Technology* 13:416–423.
- Khayyat, S. A., Akhtar, M.S. & Umar, A. 2012. ZnO nanocapsules for photocatalytic degradation of thionine. *Materials Letters* 81:239–241.
- Kim, D., Min, K., Lee, J., Park, J.H. & Chun, J.H. 2006. Influences of surface capping on particle size and optical characteristics of ZnS:Cu nanocrystals. *Materials Science and Engineering B* 131:13-17.
- Kim, K. K., Kim, D., Kim, S. K., Park, S. M. & Song, J. K. 2011. Formation of ZnO nanoparticles by laser ablation in neat water. *Chemical Physics Letters* 511: 116–120.
- Kim, K. S., Zhao, Y., Jang, H., Lee, S. Y., Kim, J.M., Kim, K. S., Ahn, J.H., Kim, P., Choi, J.Y. & Hong, B. H. 2009. Large-scale pattern growth of graphene films for stretchable transparent electrodes. *Nature* 457:706-710.

- Kim, K.D. & Kim, H.T. 2002. Formation of Silica Nanoparticles by Hydrolysis of TEOS Using a Mixed Semi-Batch/Batch Method. *Journal of Sol-Gel Science and Technology* 25:183-189.
- Kim, K.D., Choi, D.W., Choa, Y.-H. & Kim, H.T. 2007. Optimization of parameters for the synthesis of zinc oxide nanoparticles by Taguchi robust design method. *Colloids and Surfaces A – Physicochemical and Engineering Aspects* 31:170-173.
- Kitture, R., Koppikar, S. J., Ruchika, K. G. & Kale, S.N. 2011. Catalyst efficiency, photostability and reusability study of ZnO nanoparticles in visible light for dye degradation. *Journal of Physics and Chemistry of Solids* 72:60–66.
- Klingshrin, C., 2007. ZnO: Material, Physics and Applications. *A European Journal of Chemical Physics and Physical Chemistry* 8: 782-803.
- Kong, T., Chen, Y., Ye, Y., Zhang, K., Wang, Z., Wang, X. 2009. An amperometric glucose biosensor based on the immobilization of glucose oxidase on the ZnO nanotubes. *Sensors and Actuators B* 138:344–350.
- Korbahti, B.K. & Rauf, M.A. 2008. Response surface methodology (RSM) analysis of photoinduced decoloration of toluidine blue. *Chemical Engineering Journal* 136:25–30.
- Korbahti, B.K. & Rauf, M.A. 2009. Determination of optimum operating conditions of carmine decoloration by UV/H₂O₂ using response surface methodology. *Journal of Hazardous Materials* 161:281–286.
- Krishnakumar, B. & Swaminathan, M. 2010. Solar photocatalytic degradation of Acid Black 1 with ZnO. *Indian Journal of Chemistry* 49:1035-1040.
- Krishnan, C. V., Chen, J., Burger, C & Chu, B. 2006. Polymer-Assisted Growth of Molybdenum Oxide Whiskers via a Sonochemical Process. *Journal of Physical Chemistry B* 110:20182–20188.
- Kumar, S. & Sahare, P.D. 2012. Observation, of band gap and surface defects of ZnO nanoparticles synthesized via hydrothermal route at different reaction temperature. *Optics Communications* 285:5210–5216.
- Kundu, T. K., Karak, N., Barik, P. & Saha, S. 2011. Optical Properties of ZnO Nanoparticles Prepared by Chemical Method Using Poly (Vinyl Alcohol) (PVA) as Capping Agent. *International Journal of Soft Computing and Engineering* 1:19-24.
- Kuo, W. S. & Chen, W.Y. 2012. Solar Photocatalytic Degradation of Azo Dye in Aqueous TiO₂ Suspension Assisted by Fresnel Lens. *International Journal of Photoenergy* 2012:303586-303593.

- Kusic, H., Koprivanac, N. & Bozic, A.L. 2011. Treatment of chlorophenols in water matrix by UV/ferrioxalate system: Part I. Key process parameter evaluation by response surface methodology. *Desalination* 279:258–268.
- Labuayai, S., Promarak, V. & Maensiri, S. 2009. Synthesis and optical properties of nanocrystalline ZnO powders prepared by a direct thermal decomposition route. *Applied Physics A-Materials Science & Processing* 94:755-761.
- Lathasree, S., Nageswara, R.A., Sivasnkar, B., Sadasivam, V. & Rengaraj, K. 2004. Heterogeneous photocatalytic mineralization of phenols in aqueous solutions. *Journal of Molecular Catalysis A: Chemical* 223:101–105.
- Lee, J., Park, S., Park, H., Lee, J., Kim, H. & Chung, Y. 2009. photocatalytic degradation of TOC from aqueous phenol solution using combusted ZnO nanopowders. *Journal of Electroceram* 22:100-113.
- Lee, W., Sohn, H.G. & Myoung, J.M. 2004. Prediction of the structural performance of ZnO nanowires grown on GaAs (001) substrates by metalorganic chemical vapor deposition (MOCVD). *Materials Science Forum* 449–452:1245–1248.
- Legrini, O., Oliveros, E. & Braun, A.M. 1993. Photochemical processes for water treatment. *Chemical Reviews* 93:671–698.
- Lepkov'a, K., Clohessy, J. & Cunnane, V. J. 2007. The pH-controlled synthesis of a gold nanoparticle/polymer matrix via electrodeposition at a liquid–liquid interface. *Journal of Physics: Condensed Matter* 19:375106 -375118.
- Li, M., Pokhrel, S., Jin, X., Mädler, L., Damoiseaux, R. & Hoek, E.M. 2011. Stability, bioavailability, and bacterial toxicity of ZnO and iron-doped ZnO nanoparticles in aquatic media. *Environmental Science & Technology* 45:755-761.
- Li, Y., Xub, L., Li, X., Shen, X. & Wang, A. 2010. Effect of aging time of ZnO sol on the structural and optical properties of ZnO thin films prepared by sol–gel method. *Applied Surface Science* 256:4543–4547.
- Lin, G., Yunliang, J., Huibin, X., Ziyu, W. & Paul, S. 2003. Synthesis and evolution of rod-like nano-scaled $\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ whiskers to ZnO nanoparticles. *Journal of Materials Chemistry* 13:754-757.
- Lin, S.-S., Huang, J.-L. & Sajgalik, P. 2005. The properties of Ti-doped ZnO films deposited by simultaneous RF and DC magnetron sputtering. *Surface & Coatings Technology* 191:286 – 292.
- Liqiang, J., Dejun, W., Baiqi, W., Shudan, L., Baifu, X., Honggang, F. & Jiazhong, S., 2006. Effects of noble metal modification on surface oxygen composition, charge separation and photocatalytic activity of ZnO nanoparticles. *Journal of Molecular Catalysis A: Chemical* 244:193-200.

- Liu, E., Xiao, P., Chen, J.S., Lim, B.C. & Li, L. 2008. Ni doped ZnO thin films for diluted magnetic semiconductor materials. *Current Applied Physics* 8:408-411.
- Liu, G., Zhang, X., Xu, Y., Niu, X., Zheng, L. & Ding, X. 2005. The preparation of Zn²⁺-doped TiO₂ nanoparticles by sol-gel and solid phase reaction methods respectively and their photocatalytic activities. *Chemosphere* 59:1367-1371.
- Liu, H., Yang, J., Hua, Z., Zhang, Y., Yang, L., Xiao, L. & Xie, Z. 2010. The structure and magnetic properties of Cu-doped ZnO prepared by sol-gel method. *Applied Surface Science* 256: 4162-4165.
- Liu, Y. S., Luo, W. Q., Li, R. F., Zhu, H. M. & Chen, X. Y. 2009. Near-infrared luminescence of Nd³⁺ and Tm³⁺ ions doped ZnO nanocrystals. *Optics Express* 17:9748-9753.
- Liu, Y., Li, R., Luo, W., Zhu, H. & Chen, X. 2010a. Optical Spectroscopy of Sm³⁺ and Dy³⁺-Doped ZnO Nanocrystals. *Spectroscopy Letters* 43:343-349.
- Liu, Y., Luo, W., Li, R. & Chen, X. 2010b. Optical Properties of Nd³⁺ Ion-Doped ZnO Nanocrystals. *Journal of Nanoscience and Nanotechnology* 10: 1871-1876.
- Liu, Y., Yang, J., Guan, Q., Yang, L., Zhang, Y., Wang, Y., Feng, B., Cao, J., Liu, X., Yang, Y. & Wei, M. 2009. Effects of Cr-doping on the optical and magnetic properties in ZnO nanoparticles prepared by sol-gel method. *Journal of Alloys and Compounds* 486: 835-838.
- Liu, J., Xu, L., Wei, B., Lv, W., Gao, H. & Zhang, X. 2011. One-step hydrothermal synthesis and optical properties of aluminium doped ZnO hexagonal nanoplates on a zinc substrate. *CrystEngComm* 13:1283-1286.
- Lizama, C., Freer J., Baeza, J. & Mansilla, H.D. 2002. Optimized photodegradation of reactive blue 19 on TiO₂ and ZnO suspensions, *Catalysis Today* 76:235-246.
- Lu, Y., Wang, L., Wang, D., Xie, T., Chen, L. & Lin, Y. 2011. A comparative study on plate-like and flower-like ZnO nanocrystals surface photovoltage property and photocatalytic activity. *Materials Chemistry and Physics* 129: 281-287.
- Luo, J.T., Yang, Y.C., Zhu, X.Y., Chen, G., Zeng F. & Pan F. 2010. Enhanced electromechanical response of Fe-doped ZnO films by modulating the chemical state and ionic size of the Fe dopant. *Physical Review B* 82:014116-014123.
- Mahpeykar, S. M., Koohsorkhi, J. & Ghafoori-fard H. 2012. Ultra-fast microwave-assisted hydrothermal synthesis of long vertically aligned ZnO nanowires for dye-sensitized solar cell application. *Nanotechnology* 23:165602-165609.

- Malato, S., Blanco, J., Vidal, A. & Richter, C. 2002. Photocatalysis with solar energy at a pilot-plant scale: an overview. *Applied Catalysis B: Environmental* 37: 1-15.
- Malato, S., Fernández-Ibañez, P., Maldonado, M.I., Blanco, J. & Gernjak, W. 2009. Decontamination and disinfection of water by solar photocatalysis: Recent overview and trends. *Catalysis Today* 147:1-59.
- Marc P., Verónica G.-M., Baños, M. A., Giménez, J. & Esplugas, S. 2004. Degradation of chlorophenols by means of advanced oxidation processes: a general review. *Applied Catalysis B: Environmental* 47:219-256.
- Masters, G. M. 2004. *Renewable and efficient electric power systems*. New Jersey : John Wiley & Sons.
- Masuda, Y., Kinoshita, N. & Koumoto, K. 2007. Morphology control of ZnO crystalline particles in aqueous solution. *Electrochimica Acta* 53:171-174.
- Mehos, M. & Turchi, C. 1992. Measurement and analysis of near ultraviolet solar radiation. *Solar Engineering* 1: 51-55.
- Mehrotra R.C. 1992. Precursors for aerogels. *Journal of Non-Crystalline Solids* 145:1-10.
- Mijin, D., Savić, M., Snežana, P., Smiljanić, A., Glavaški, O., Jovanović, M. & Petrović, S. 2009. A study of the photocatalytic degradation of metatiron in ZnO water suspensions. *Desalination* 249:286-292.
- Milner, C. & Goulder, R. 1986. Comparative toxicity of chlorophenols, nitrophenols, and phenoxyalkanoic acids to fresh water bacteria. *Bulletin of Environmental Contamination and Toxicology* 37:714-718.
- Minghua, Z., Yu, J. & Cheng, B. 2006. Effects of Fe-doped on the photocatalytic activity of mesoporous TiO₂ powder prepared by an ultrasonic method. *Journal of Hazardous Materials* 137:1838-1847.
- Mir, N., Salavati-Niasari, M. & Davar, F. 2012. Preparation of ZnO nanoflowers and Zn glycerolate nanoplates using inorganic precursors via a convenient route and application in dye sensitized solar cells. *Chemical Engineering Journal* 181:779-789.
- Mishra, A.K. & Das, D. 2010. Investigation on Fe-doped ZnO nanostructures prepared by a chemical route. *Materials Science and Engineering B* 171:5-10.
- Montgomery, D. C. 1991. *Design and Analysis of Experiments*, Third Edition. USA: John Wiley & Sons.

- Morales, R., Ortiz M.C., Sarabia, L.A. & Sánchez, M.S. 2011. D-optimal designs and N-way techniques to determine sulfathiazole in milk by molecular fluorescence spectroscopy. *Analytica Chimica Acta* 707:38-46.
- Morkoc, H. & Özgür, Ü. 2009. *Zinc Oxide Fundamentals, Materials and Device Technology*. Wiley-VCH Verlag GmbH & Co. KGaA.
- Morris, M.D.A. 2000. Class of Three-Level Experimental Designs for Response Surface Modeling. *Technometrics* 42:111-121.
- Muhammad, S., Hussain, S. T., Waseem, M., Naeem, A., Hussain, J. & Jan, M. T. 2012. Surface charge properties of zirconium dioxide. *Iranian Journal of Science & Technology* A4: 481-486.
- Musat, V., Fortunato, E., Purica, M., Mazilu, M., Rego, A., Diaconu, B. & Busani, T. 2012. Multifunctional zinc oxide nanostructures for a new generation of devices. *Materials Chemistry and Physics* 132:339-346.
- Myers, R.H. & Montgomery, D.C. 2002. *Response Surface Methodology. Process and Products Optimization Using Designed Experiments*. New York: John Wiley & Sons, Inc.
- Naeem, M., Qaseem, S., Gul, I. H. & Maqsood, A. 2010. Study of active surface defects in Ti doped ZnO nanoparticles. *Journal of Applied Physics* 107:124303:124310.
- Nair, M. G., Nirmala, M., Rekha, K. & Anukaliani, A. 2011. Structural, optical, photocatalytic and antibacterial activity of ZnO and Co doped ZnO nanoparticles. *Materials Letters* 65:1797-1800.
- Navarro, S., Fenoll, J., Vela, N., Ruiz, E. & Navarro, G. 2009. Photocatalytic degradation of eight pesticides in leaching water by use of ZnO under natural sunlight. *Journal of Hazardous Materials* 172:1303-1310.
- Nejati, K., Rezvani, Z. & Pakizevand, R. 2011. Synthesis of ZnO Nanoparticles and Investigation of the Ionic Template Effect on Their Size and Shape. *International Nano Letters* 1:75-81.
- Ni, L., Wang, L., Shao, B., Wang, Y., Zhang, W. & Jiang, Y. 2011. Synthesis of Flower-like Zinc Oxalate Microspheres in Ether-water Bilayer Refluxing Systems and Their Conversion to Zinc Oxide Microspheres. *Journal of Materials Science & Technology* 27:563-569.
- Nieto, J., Freer, J., Contreras, D., Candal, R.J., Sileo, E.E. & Mansilla, H.D. 2008. Photocatalyzed degradation of flumequine by doped TiO₂ and simulated solar light. *Journal of Hazardous Materials* 155:45-50.
- Oehlert, G.W. 2000. *Design and Analysis of Experiments: Response Surface Design*, W.H. Freeman and Company, New York.

- Oha, E., Choib, H., Jungc, S., Cho, S., Kim, J. C., Lee, K., Kang, S., Kim, J., Yun, J. & Jeonga S. 2009. High-performance NO₂ gas sensor based on ZnO nanorod grown by ultrasonic irradiation. *Sensors and Actuators B: Chemical* 141:239–243.
- Ohno, T. & Tokeda, K. 2003. Synergism between rutile and anatase TiO₂ particles in photocatalytic oxidation of naphthalene. *Applied catalysis A: general* 244:383–391.
- Ollis, D. F. & Al-Elkabi, H. 1993. *Photocatalytic Purification and Treatment of Water and Air*. Netherlands: Elsevier. Amsterdam.
- Omidi, A., Habibi-Yangjeh, A. & Pirhashemi, M. 2013. Application of ultrasonic irradiation method for preparation of ZnO nanostructures doped with Sb³⁺ ions as a highly efficient photocatalyst. *Applied Surface Science* 276:468–475.
- Ou, X., Wu C. & Lo, S. 2006. Photodegradation of 4-chlorophenol by uv/photocatalysts: the effect of the interparticle electron transfer process. *Reaction Kinetics and Catalysis Letters* 88:89–95.
- Ozgür, Ü., Alivov, Y. I., Liu, C., Teke, A., Reshchikov, M. A., Doğan, S., Avrutin, V., Cho, S.J. & Morkoc, H. 2005. A comprehensive review of ZnO materials and device. *Journal of Applied Physics* 98: 041301–041403.
- Padmanabhan, P.V.A., Sreekumar, K.P., Thiyagarajan, T.K., Satpute, R.U., Bhanumurthy, K., Sengupta, P., Dey, G.K. & Warriar, K.G.K. 2006. Nanocrystalline titanium dioxide formed by reactive plasma synthesis. *Vacuum* 80:1252–1255.
- Pala, R. S. & Metiu, H. 2007. Modification of the Oxidative Power of ZnO (101̄0) Surface by Substituting Some Surface Zn Atoms with Other Metals. *Journal of Physical Chemistry C* 111:8617–8622.
- Palmer, F., Eggins, B. & Coleman, H. 2002. The Effect of Operational Parameters on the Photocatalytic Degradation of Humic Acid. *Journal of Photochemistry and Photobiology A: Chemistry* 148:137–143.
- Palominos, R.A., Mondaca, M.A., Giraldo, A., Peñuela, G., Pérez-Moya, M. & Mansilla, H.D. 2009. Photocatalytic oxidation of the antibiotic tetracycline on TiO₂ and ZnO suspensions. *Catalysis Today* 144:100–105.
- Pan, L., Qiu, Y., Chen, T., Lin, J., Chi, Y., Su, M., Zhao, A. & Jia, W. 2010. An optimized procedure for metabonomic analysis of rat liver tissue using gas chromatography/time-of-flight mass spectrometry. *Journal of Pharmaceutical and Biomedical Analysis* 52:589–596.

- Panda, A.B., Glaspell, G. & El-Shall, M.S. 2006. Microwave synthesis of highly aligned ultramarrows semiconductor rods and wires. *Journal of the American Chemical Society* 128:2790-2791.
- Pandiyar, T., Rivas, O. M., Mart'inez, J. O., Amezcua, G. B. & Mart'inez-Carrillo, M.A. 2002. Comparison of methods for the photochemical degradation of chlorophenols. *Journal of Photochemistry and Photobiology A: Chemistry* 146:149–155.
- Panigrahy, B., Aslam M. & Bahadur, D. 2012. Effect of Fe-doping concentration on optical and magnetic properties of ZnO nanorods. *Nanotechnology* 23:115601-115607.
- Paola, A. D., Bellardita, M., Marc, G., Palmisano, L., Parrino, F. & Amadelli, R. 2011. Preparation of Sm-loaded brookite TiO₂ photocatalysts. *Catalysis Today* 161:35-40.
- Pardeshi, S. K. & Patil, A. B. 2009. Solar photocatalytic degradation of resorcinol a model endocrine disrupter in water using zinc oxide. *Journal of Hazardous Materials* 163:403–409.
- Pardeshi, S.K. & Patil, A.B. 2008. A simple route for photocatalytic degradation of phenol in aqueous zinc oxide suspension using solar energy. *Solar Energy* 82:700-705.
- Parent, Y., Blake, D., Magrini-Bair, K., Lyons, C., Turchi, C., Watt, A., Wolfrum, E. & Prairie, M. 1996. Solar photocatalytic processes for the purification of water: state of development and barriers to commercialization. *Solar Energy* 56:429–437.
- Parida, K.M. & Parija, S. 2006. Photocatalytic degradation of phenol under solar radiation using microwave irradiated zinc oxide. *Solar Energy* 80:1048–1054.
- Pathak, T. K. & Purohit, L.P. 2013. Structure and Room Temperature Ferromagnetism of Ni²⁺-doped ZnO Nanoparticles Prepared by Sol-gel Process. *International Journal of Basic and Applied Sciences* 2:29-31.
- Pearson, S.J., Norton, D.P., Ipa, K., Heo, Y.W. & Steiner, T. 2005. Recent progress in processing and properties of ZnO. *Progress in Materials Science* 50:293–340.
- Pokropivny, V.V. & Skorokhod V.V. 2007. Classification of nanostructures by dimensionality and concept of surface forms engineering in nanomaterial science. *Materials Science and Engineering C* 27:990–993.
- Poulios, I., Makri, D. & Prohaska, X. 1999. Photocatalytic treatment of olive milling waste water: oxidation of protocatechuic acid. *Global NEST: The International Journal* 1:55–62.

- Pozzo, R. L., Baltana's, M. A. & Cassano, A. E. 1997. Supported titanium oxide as photocatalyst in water de contamination: state of the art. *Catalyst Today* 39:219-3231.
- Pradhan, D. & Leung, K. T. 2008. Vertical Growth of Two-Dimensional Zinc Oxide Nanostructures on ITO-Coated Glass: Effects of Deposition Temperature and Deposition Time. *The Journal of Physical Chemistry C* 112:1357-1364.
- Priya, S.S., Premalatha, M. & Anantharaman, N. 2008. Solar Photocatalytic Treatment of Phenol Wastewater Potential, challenges and opportunities. *International Journal of Applied Engineering Research* 3:36-41.
- Protasova, L. N., Rebrov, E. V., Choy, K. L., Pung, S. Y., Engels, V., Cabaj, M., Wheatley, A. E. H. & Schouten, J. C. 2011. ZnO based nanowires grown by chemical vapour deposition for selective hydrogenation of acetylene alcohols. *Catalysis Science & Technology* 1:768-777.
- Qamar, M. & Muneer, M. 2005. Comparative photocatalytic study of two selected pesticide derivatives, indole-3-acetic acid and indole-3-butyric acid in aqueous suspensions of titanium dioxide. *Journal of Hazardous Materials* 120:219-27.
- Rabindranathan, S., Devipriya, S. & Yesodharan, S. 2003. Photocatalytic degradation of phosphamidon on semiconductor oxides. *Journal of Hazardous Materials* 102:217-229.
- Ram, M., Andreescu, E. S. & Hanming, D. 2011. *Nanotechnology for Environmental Decontamination*. USA: McGraw Hill Professional.
- Rao, A. N., Sivasankar, B. & Sadasivam, V. 2009. Kinetic study on the photocatalytic degradation of salicylic acid using ZnO catalyst. *Journal of Hazardous Materials* 166:1357-1361.
- Rao, N.N., Dubey, A.K., Mohanty, S., Khare, P., Jain, R. & Kaul, S.N. 2003. Photocatalytic degradation of 2-chlorophenol: a study of kinetics. Intermediates and biodegradability. *Journal of Hazardous Materials B* 101:301-314.
- Rauf, M.A., Marzouki, N. & Korbahti, B.K. 2008. Photolytic decolorization of Rose Bengal by UV/H₂O₂ and data optimization using response surface method. *Journal of Hazardous Materials* 159:602-609.
- Ravichandran, L., Selvam, K. & Swaminathan, M. 2007. Effect of oxidants and metal ions on photodefluoridation of pentafluorobenzoic acid with ZnO. *Separation and Purification Technology* 56:192-198.
- Rekha, K., Nirmala, M., Nair, M. G. & Anukaliani, A. 2010. Structural, optical, photocatalytic and antibacterial activity of zinc oxide and manganese doped zinc oxide nanoparticles. *Physica B: Condensed Matter* 405:3180-3185.

- Rodriguez, J.A. & Fernandez-Garcia M. 2007. *Synthesis, properties and applications of oxide nonmaterials*. Wiley: Hoboken.
- Roe, A. J., O'Byrne, C., McLaggan, D. & Booth, I. R. 2002. Inhibition of *Escherichia coli* growth by acetic acid: a problem with methionine biosynthesis and homocysteine toxicity. *Microbiology* 148:2215–2222.
- Safaei, M., Sarraf-Mamoory, R., Rashidzadeh, M. & Manteghian, M. 2010. A Plackett–Burman design in hydrothermal synthesis of TiO₂-derived nanotubes. *Journal of Porous Materials* 17:719–726.
- Sakkas, V. A., Islam, Md. A., Stalikas, C. & Albanis, T. A. 2010. Photocatalytic degradation using design of experiments: A review and example of the Congo red degradation. *Journal of Hazardous Materials* 175: 33–44.
- Sakthivel, S., Neppolian, B., Shankar, M.V., Arabindoo, B., Palanichamy, M. & Murugesan, V. 2003. Solar photocatalytic degradation of azo dye: comparison of photocatalytic efficiency of ZnO and TiO₂. *Solar Energy Materials & Solar Cells* 77:65–82.
- Salimon, J., Abdullah B.M. & Salih, N. 2011. Hydrolysis optimization and characterization study of preparing fatty acids from *Jatropha curcas* seed oil. *Chemistry Central Journal* 5:67–76.
- Salimon, J., Abdullah B.M. & Salih, N. 2012. Selectively increasing of polyunsaturated (18:2) and monounsaturated (18:1) fatty acids in *Jatropha curcas* seed oil by crystallization using D-optimal design. *Chemistry Central Journal* 6:65–80.
- Samah, M., Merabet, S., Bouguerra, M., Bouhelassa, M., Ouhenia, S. & Bouzaza, A. 2011. Photooxidation process of indole in aqueous solution with ZnO Catalyst: Study and optimization. *Kinetics and Catalysis* 52:34–39.
- Sanchez, C., Boissiere, C., Coupe, A., Goettmann, F., Grosso, D.; Julian, B., Llusar, M. & Nicole, L. 2005. Design of functional nano-structured inorganic and hybrid materials. *Studies in Surface Science and Catalysis* 156:19–36.
- Sarawuth, L., Vinich, P. & Santi, M. 2009. Synthesis and optical properties of nanocrystalline ZnO powders prepared by a direct thermal decomposition route. *Applied Physics A* 94:755–761.
- Sato K. & Yoshida H. 2002. First principles design for semiconductor Spintronics. *Semiconductor Science and Technology* 17:367–376.
- Schimmoeller, B., Pratsinis S.E. & Baiker, A. 2011. Flame Aerosol Synthesis of Metal Oxide Catalysts with Unprecedented Structural and Catalytic Properties. *ChemCatChem* 3:1234–1256.

- Seetawan, U., Jugsujinda, S., Seetawan, T., Euvananont, C., Junin, C., Thanachayanont, C., Chainaronk, P. & Amornkitbamrung, V. 2011. Effect of annealing temperature on the crystallography, particle size and thermopower of bulk ZnO. *Solid State Sciences* 13:1599-1603.
- Sekiguchi, T., Haga, K., & Inaba, K. 2000. ZnO films grown under the oxygen-rich condition. *Journal of Crystal Growth* 214-215:68-71.
- Shafaei, A., Nikaza, M. & Arami, M. 2010. Photocatalytic degradation of terephthalic acid using titania and zinc oxide photocatalysts: comparative study. *Desalination* 252, 8-16.
- Sheng, X., Zhao, Y., Zhai, J., Hiang, L. & Zhu, D. 2007. Electro-hydrodynamic fabrication of ZnO-based dye sensitized solar cells. *Applied Physics A* 87:715-719.
- Shifu, C., Wei, Z., Wei, L. & Sujuan, Z. 2009. Perpartion, characterization and activity evalution of p-n junction photocatalyt p-NiO/N-ZnO. *Journal Sol Gel Scince and Technology* 50:387-396.
- Shinde, S. S., Shinde, P. S., Bhosale, C. H. & Rajpure, K. Y. 2011. Zinc oxide mediated heterogeneous photocatalytic degradation of organic species under solar radiation. *Journal of Photochemistry and Photobiology B* 104: 425–433.
- Shukla, P., Wang, S., Ang, H.M. & Tadé, M. O. 2010. Photocatalytic oxidation of phenolic compounds using zinc oxide and sulphate radicals under artificial solar light. *Separation and Purification Technology* 70:338–344.
- Siddiquey, I. A., Furusawa, T., Sato, M., Bahadur, N. M., Alam, M. M. & Suzuki, N. 2012. Sonochemical synthesis, photocatalytic activity and optical properties of silica coated ZnO nanoparticles. *Ultrasonics Sonochemistry* 19:750–755.
- Sing, S.W., Everett, D.H., R. Moscou, A.W., Pierotti, R.A., Rouquerol, J. & Siemieniewska, T. 1985. Reporting physisorption data for gas/soild system with seical reference to the determination of surface area and porosity. *Pure Applied Chemistry* 57:603-619.
- Singh, A.K., Viswanath, V. & Janu, V.C. 2009. Synthesis, effect of capping agents, structural, optical and photoluminescence propertiesof ZnO nanoparticles. *Journal of Luminescence* 129:874–878.
- Singh, L. R., Ningthoujam, R.S., Sudarsan, V., Singh, S. D. & Kulshreshtha, S.K. 2008. Probing of surface Eu^{3+} ions present in ZnO:Eu nanoparticles bycovering ZnO:Eu core with Y_2O_3 shell: Luminescence study. *Journal of Luminescence* 128:544–1550.
- Singh, N., Dhruvashi, Kaur, D., Mehra R. M. & Kapoor A. 2012. Effect of ageing in structural properties of ZnO nanoparticles with pH variation for application in solar cells. *The Open Renewable Energy Journal* 5:15-18.

- Singh, N., Mehra, R.M. & Kapoor, A. 2011. Synthesis and Characterization of ZnO Nanoparticles. *Journal of Nano- and Electronic Physics* 3:132-140.
- Skorokhod, V., Ragulya, A. & Uvarova, I. 2001. *Physico-chemical kinetics in nanostructured systems*. Academperiodica, Kiev, p. 180.
- Sobana, N. & Swaminathan, M. 2007. The effect of operational parameters on the photocatalytic degradation of acid red 18 by ZnO. *Separation and Purification Technology* 56:101-107.
- Srivastava, A.K., Deepa, M., Bahadur, N. & Goyat, M.S. 2009. Influence of Fe doping on nanostructures and photoluminescence of sol-gel derived ZnO. *Materials Chemistry and Physics* 114:194-198.
- Stanković, A., Veselinović, L., Škapin, S. D., Marković, S. & Uskoković, D. 2011. Controlled mechanochemically assisted synthesis of ZnO nanopowders in the presence of oxalic acid. *Journal of Materials Science* 46:3716-3724.
- Stumm, W. 1992. *Chemistry of the Solid-Water Interface*, John Wiley & Sons, New York, USA.
- Sun, H., Feng, X., Wang, S., Ang, H. M. & Tadém M.O. 2011. Combination of adsorption, photochemical and photocatalytic degradation of phenol solution over supported zinc oxide: Effects of support and sulphateoxidant. *Chemical Engineering Journal* 170:270-277.
- Suttiaponparnit, K., Jiang, J., Sahu, M., Suvachittanont, S., Charinpanitkul, T. & Biswas, P. 2011. Role of surface area, primary particle size, and crystal phase on Titanium dioxide nanoparticle dispersion properties. *Nanoscale Research Letters* 6:27-35.
- Tabatabaei, S. M., Dastmalchi, S., Mehrizad, A. & Gharbani, P. 2011. Enhancement of 4-nitrophenol ozonation in water by nano ZnO catalyst. *Iranian Journal of Environmental Health Science & Engineering* 8:363-372.
- Tan, B., Long, X., Peng, R., Li, H., Jin, B., Chu, S. & Dong, H. 2010. Two important factors influencing shock sensitivity of nitro compounds: Bond dissociation energy of X-NO₂ (X = C, N, O) and Mulliken charges of nitro group. *Journal of Hazardous Materials* 183:908-912.
- Teofilo, R.F. & Ferreira, M.M.C. 2006. Chemometrics II: spreadsheets for experimental design calculations, a tutorial. *Química Nova* 29:338-350.
- Tian, Z.Y., Chen, Y., Yang, W.S., Yao, J.N., Zhu, L.Y. & Shuai, Z.G. 2004. Low-Dimensional Aggregates from Stilbazolium-Like Dyes. *Angewandte Chemie* 43:4060-403.

- Tong, T., Zhang, J., Tian, B., Chen, F. & He, D. 2008. Preparation of Fe³⁺-doped TiO₂ catalysts by controlled hydrolysis of titanium alkoxide and study on their photocatalytic activity for methyl orange degradation. *Journal of Hazardous Materials* 155:572-579.
- Toor, A., Verma, A., Jotshi, C., Bajpai, P. & Singh, V. 2005. photocatalytic degradation of 3,4 -dichlorophenol using TiO₂ in shallow pond slurry reactor. *Indian journal of chemical Technology* 12:75-81.
- Torres-Lapasió J.R., Pous-Torres S., Baeza-Baeza J.J. & García-Álvarez-Coque, M.C. 2011. Optimal experimental designs in RPLC at variable solvent content and pH based on prediction error surfaces. *Analytical and Bioanalytical Chemistry* 400:1217-1230.
- Tseng, Y., Lin, Y., Chang, H., Chen, Y, Liu, C. & Zou, Y. 2012. Effects of Ti content on the optical and structural properties of the Ti-doped ZnO nanoparticles. *Journal of Luminescence* 132:491–494.
- Umar, A., Karunakaran, B., Suh, E.K. & Hahn, Y. B. 2006. Structural and optical properties of single-crystalline ZnO nanorods on silicon by thermal evaporation. *Nanotechnology* 17:4072-4077.
- Urban, J., Svec, F. & Frechet, J.M.J. 2010. Hypercrosslinking: New approach to porous polymer monolithic capillary columns with large surface area for the highly efficient separation of small molecules. *Journal of Chromatography A* 1217:8212-8221.
- Uthirakumar, P. & Hong, C.H. 2009. Effect of annealing temperature and pH on the morphology and optical properties of highly dispersible ZnO nanoparticles. *Materials Characterization* 60:1305-1310.
- Uthirakumar, P., Lee, Y., Suh, E. & Hong, C. 2006. ZnO nanoballs synthesized from a single molecular precursor via non-hydrolytic solution route without assistance of base, surfactant, and template etc. *Physics Letters A* 359:223–226.
- Vayssieres, L., Keis, K., Lindquist, S. E. & Hagfeldt, A. 2001. Purpose-built anisotropic metal oxide material: 3D highly oriented microrod array of ZnO. *The Journal of Physical Chemistry B* 105:3350–3352.
- Venkatesham, V., Gattumane, M. M., Suggala, V. S. & Halugondanahalli, S. P. 2012. Photocatalytic degradation of methylene blue using a zinc oxide-cerium oxide catalyst. *European Journal of Chemistry*, 3:191-195.
- Veschueren, H.K. 1983. *Handbook of environmental data on organic chemicals*. VNR, New York.
- Vialaton, D. & Richard, C. 2002. Phototransformation of aromatic pollutants in solar light: photolysis versus photosensitized reactions under natural water conditions. *Aquatic Sciences* 64:207–215.

- Vijayana, P., Mahendirana, C., Suresha, C. & Shanthi, K., 2009. Photocatalytic activity of iron doped nanocrystalline titania for the oxidative degradation of 2,4,6-trichlorophenol. *Catalysis Today* 141:220-224.
- Vione, D., Minero, C., Maurino, V., Carlotti, M., Picatotto, T. & Pelizzetti, E. 2005. Degradation of phenol and benzoic acid in the presence of a TiO_2 -based heterogeneous photocatalyst. *Applied Catalysis B: Environmental* 58:79-88.
- Vora, J. J., Chauhan, S. K., Parmar, K.C., vasava, S.B, Sharma, S. & Bhutadiya, L.S. 2009. Kinetic Study of Application of ZnO as a Photocatalyst in Heterogeneous Medium. *E-Journal of Chemistry* 6:531-536.
- Wageh, S., Shu-Man, L., Tian-You, F. & Xu-Rong, X. 2003. Optical properties of strongly luminescing mercaptoacetic-acid-capped ZnS nanoparticles. *Journal of Luminescence* 102:768-773.
- Wahab R., Mishra, A., Yun, S., Kim, Y.S. & Shin, H.S. 2010. Antibacterial activity of ZnO nanoparticles prepared via non-hydrolytic solution route. *Applied Microbiology and Biotechnology* 87:1917-1925.
- Wahab, H. S., Bredow, T. & Aliwi, S. M. 2008. Computational modeling of the adsorption and photodegradation of 4-chlorophenol on anatase TiO_2 particles. *Journal of Molecular Structure* 86:384-90.
- Wahab, R., Hwang, I.H., Kim, Y., Musarrat, J., Siddiqui, M.A., Seod, H., Tripathy S. & H. & Shin. 2011a. Non-hydrolytic synthesis and photo-catalytic studies of ZnO nanoparticles. *Chemical Engineering Journal* 175:450-457.
- Wahab, R., Kaushik, N.K., Verma, A. K., Mishra, A., Hwang, I. H., Yang, Y., Shin, H. & Kim, Y. 2011b. Fabrication and growth mechanism of ZnO nanostructures and their cytotoxic effect on human brain tumor U87, cervical cancer HeLa, and normal HEK cells. *Journal of Biological Inorganic Chemistry* 16:431-442.
- Wahab, R., Kim, Y., & Shin, H. 2009. Synthesis, Characterization and Effect of pH Variation on Zinc Oxide Nanostructures. *Materials Transactions* 50:2092-2097.
- Wang, F. & Hu, S. 2009. Electrochemical sensors based on metal and semiconductor nanoparticles, *Microchimica Acta* 165:1-22.
- Wang, R., Xin, J. H., Y., Yang, Liu, H., Xu, L. & Hu, J. 2004. The characteristics and photocatalytic activities of silver doped ZnO nanocrystallites. *Applied Surface Science* 227:312-317.
- Wang, Z. L. 2004. Zinc oxide nanostructures: Growth, properties and applications. *Journal of Physics: Condensed Matter* 16:829-858.

- Wei, T. Y., Yeh, P. H., Lu, S. Y. & Wang, Z. L. 2009. Gigantic enhancement in sensitivity using Schottky contacted nanowire nanosensor. *Journal of the American Chemical Society* 131:17690–17695.
- Wei, Y. G., Xu, C., Xu, S., Li, C., Wu, W. Z. & Wang, Z. L. 2010. Planar waveguide-nanowire integrated three-dimensional dyesensitized solar cells. *Nano Letters* 10:2092–2096.
- Wu, C. F. J. & Hamada, M. 2000. *Design of Experiments: Planing, Analysis and Parameter Design Optimization*, John Wiley & Sons, INC., USA.
- Wu, C., Qiao, X., Chen, J., Wang, H., Tan, F. & Li, S. 2006. A novel chemical route to prepare ZnO nanoparticles. *Materials Letters* 60:1828–1832.
- Xiao, Q., Si, Z., Yu, Z. & Qiu, G. 2008. Characterization and photocatalytic activity of Sm^{3+} -doped TiO_2 nanocrystalline prepared by low temperature combustion method. *Journal of Alloys and Compounds* 450:426-231.
- Xie, Y., Cai, B., Yu, D., Shan, W. & Zhang, W. 2012. Template-guided growth of well-aligned ZnO nanocone arrays on FTO substrate. *Journal of Crystal Growth* 346: 64–68.
- Xu, C.X., Sun, X.W., Chen, B.J., Shum, P., Li, S. & Hu, X. J. 2004. Zinc oxide nanowires and nanorods fabricated by vapour-phase transport at low temperature. *Nanotechnology* 15:839-842.
- Xu, H., Zhao, Q., Yang, H. & Chen, Y. 2009. Study of magnetic properties of ZnO nanoparticles codoped with Co and Cu. *Journal of Nanoparticle Research* 11:615–621.
- Yang, L., Wang, G., Tang, C., Wang, H. & Zhang, L. 2005. Synthesis and photoluminescence of corn-like ZnO nanostructures under solvothermal-assisted heat treatment. *Chemical Physics Letters* 409:337–341.
- Yang, R. S., Qin, Y., Dai, L. M. & Wang, Z. L. 2009. Power generation with laterally packaged piezoelectric fine wires. *Nature Nanotechnology* 4:34–39.
- Yang, Y., Li, X., Chen, J., Chen, H. & Bao, X. 2003. ZnO nanoparticles prepared by thermal decomposition of b-cyclodextrin coated zinc acetate. *Chemical Physics Letters* 373:22–27.
- Yao, B. D., Chan, Y. F. & Wang, N. 2002. Formation of ZnO nanostructures by a simple way of thermal evaporation. *Applied Physics Letters* 81:757–759.
- Yin, Z., Chen, N., Dai, R., Liu, L., Zhang, X., Wang, X., Wu, J. & Chai, C. 2007. On the formation of well-aligned ZnO nanowall networks by catalyst-free thermal evaporation method. *Journal of Crystal Growth* 305: 296–301.

- Yousefi, R. & Sheini, F. 2012. Effect of chlorine ion concentration on morphology and optical properties of Cl-doped ZnO nanostructures. *Ceramics International* 38:5821–5825.
- Yu, K., Jin, Z., Liu, X., Liu, Z. & Fu, Y. 2007. Synthesis of size-tunable ZnO nanorod arrays from $\text{NH}_3\cdot\text{H}_2\text{O}/\text{ZnNO}_3$ solutions. *Materials Letters* 61:2775–2778.
- Yu, X., Meng, D., Liu, C., He, X., Wang, Y. & Xie, J. 2012. Structure and ferromagnetism of Fe-doped and Fe-and Co-codoped ZnO nanoparticles synthesized by homogeneous precipitation method. *Materials Letters* 86:112–114.
- Yu, Y., Ma, L.L., Huang, W.Y., Li, J.L., Wong, P.K. & Yu, J.C. 2005. Coating MWNTs with Cu_2O of different morphology by a polyol process. *Journal of Solid State Chemistry* 178:1488–1494.
- Yuan, H. & Zhang, Y. 2004. Preparation of well-aligned ZnO whiskers on glass substrate by atmospheric MOCVD. *Journal of Crystal Growth* 263:119–124.
- Zak, A. K., Abd. Majid, W.H., Mahmoudian, M.R., Darroudi, M. & Yousefi, R. 2013. Starch-stabilized synthesis of ZnO nanopowders at low temperature and optical properties study. *Advanced Powder Technology* 24:618–624.
- Zak, A. K., Razali, R., Abd Majid, W.H. & Darroudi, M. 2011. Synthesis and characterization of a narrow size distribution of zinc oxide nanoparticles. *International journal Nanomedicine* 6:1399–1403.
- Zeng, J., Jin, B. & Wang, Y. 2009. Facet enhanced photocatalytic effect with uniform single-crystalline zinc oxide nanodisks. *Chemical Physics Letters* 472:90–95.
- Zhang, J., Gao, D., Yang, G., Zhang, J., Shi, Z., Zhang, Z., Zhu, Z. & Xue, D. 2011. Synthesis and magnetic properties of Zr doped ZnO Nanoparticles, *Nanoscale Research Letters* 6:587–694.
- Zhang, J., Sun, L., Yin, J., Su, H., Liao, C. & Yan, C. 2002. Control of ZnO morphology via a simple solution route. *Chemistry of Materials* 14:4172–4177.
- Zhang, L., Zhao, J., Lu, H., Li L., Zheng, J., Li, H. & Zhu, Z. 2012. Facile synthesis and ultrahigh ethanol response of hierarchically porous ZnO Nanosheets. *Sensors and Actuators B* 161:209–215.
- Zhang, Y. L., Yang, Y., Zhao, J.H., Tan, R. Q., Cui, P., & Song, W. J. 2009. Preparation of ZnO nanoparticles by a surfactant-assisted complex sol-gel method using zinc nitrate. *Journal of Sol-Gel Science and Technology* 51:198–203.

- Zhang, Y., Ram, M. K., Stefanakos, E.K. & Goswami, D. Y. 2012. Synthesis, Characterization, and Applications of ZnO Nanowires. *Journal of Nanomaterials* 2012:624520-624542.
- Zhang, Z. & Zheng, H. 2009. Optimization for decolorization of azo dye acid green 20 by ultrasound and H_2O_2 using response surface methodology. *Journal of Hazardous Materials* 172:1388–1393.
- Zhou, M., Yu, J. & Cheng, B. 2006. Effects of Fe-doping on the photocatalytic activity of mesoporous TiO_2 powders prepared by an ultrasonic method. *Journal of Hazardous Materials* 137:1838–1847.



APPENDIX A

PUBLISHED PAPERS FROM THIS THESIS AND RELATED STUDY

A. List of journal publications

1. Muneer M. Ba-abbad, Abdul Amir H. Kadhum, Abu bakar Mohamad, Mohd S., Takriff, Kamaruzzaman. 2013. Visible light photocatalytic activity of Fe³⁺-doped ZnO nanoparticles prepared via sol-gel technique *Chemosphere* 91:1604-1611.
2. Muneer M. Ba-abbad, Abdul Amir H. Kadhum, Abu bakar Mohamad, Mohd S., Takriff, Kamaruzzaman. 2013. The effect of process parameters on the size of ZnO nanoparticles synthesized via the sol-gel technique, *Journal of Alloys and Compounds* 550:63-70
3. Muneer M. Ba-abbad, Abdul Amir H. Kadhum, Abu bakar Mohamad, Mohd S., Takriff, Kamaruzzaman. 2013. Optimization of process parameters using D-optimal design for synthesis of ZnO nanoparticles via sol-gel technique, *Journal of Industrial and Engineering Chemistry* 19:99-105.
4. Muneer M. Ba-abbad, Abdul Amir H. Kadhum, Abu bakar Mohamad, Mohd S., Takriff, Kamaruzzaman. 2013. Photocatalytic degradation of chlorophenols under direct solar radiation in the presence of ZnO catalyst, *Research on Chemical Intermediates* 39:1981-1996.
5. Muneer M. Ba-abbad, Abdul Amir H. Kadhum, Abu bakar Mohamad Mohd S., Takriff, Kamaruzzaman Sopian, Salmin S. Al-Shamali. 2013. Kinetics transformation of anatase to rutile phase for titanium dioxide nanoparticles prepared by sol-gel method. *Materials Science Forum* 756:11-15.
6. Muneer M. Ba-abbad, Abdul Amir H. Kadhum, Ahmed. A. Al-Amiery, Abu bakar Mohamad, Mohd S., Takriff. 2012. Toxicity evaluation for low concentration of chlorophenols under solar radiation using zinc oxide (ZnO) nanoparticles, *International Journal of Physical* 7:48 – 52.
7. Muneer M. Ba-abbad, Abdul Amir H. Kadhum, Abu bakar Mohamad Mohd S., Takriff, Kamaruzzaman Sopian. 2012. Synthesis and Catalytic Activity of TiO₂ Nanoparticles for Photochemical Oxidation of Concentrated Chlorophenols under Direct Solar Radiation. *International Journal of Electrochemical Science* 7:4871 – 4888.
8. Muneer M. Ba-abbad, Abdul Amir H. Kadhum, Abu bakar Mohamad, Mohd S., Takriff, Ramzi, T. T. Jalgham. 2012. Comparative Study of the Adsorption Mechanism and Photochemical Oxidation of Chlorophenols on a TiO₂

Nanocatalyst. *International Journal of Electrochemical Science* 7:11363-11376.

9. Ahmed, Y. Musa, Muneer M. Ba-abbad, Abdul Amir H. Kadhum, Abu bakar Mohamad. 2012. Photodegradation of chlorophenolic compounds using zinc oxide as photocatalyst: experimental and theoretical studies. *Research on Chemical Intermediates* 38:995-1005.
10. Mohd S. Takriff, Muneer M. Ba-abbad, Abdul Amir h. Kadhum, Abu bakar Mohamad, Kamaruzzaman Sopian. 2011. Solar Photocatalytic Degradation of 2,4-Dichlorophenol by TiO₂ Nanoparticle Prepared by Sol-gel Method. *Advanced Materials Research* 233-235:3032-3035.

B. List of conference publications

- 1- Muneer M. Ba-abbad, Abdul Amir H. Kadhum, Abu bakar Mohamad Mohd S. solar photocatalytic degradation of phenol in water solution using TiO₂ catalysts. 2009. Proceeding of International Conference on sustainable development for water and wastewater treatment, Yogyakarta, Indonesia, pp.298.
- 2- Muneer M. Ba-abbad, Abdul Amir H. Kadhum, Abu bakar Mohamad Mohd S., Takriff. 2009. Solar Photocatalytic Degradation Of 2-Chlorophenol Using Zinc Oxid. Proceedings of the Regional Engineering Postgraduate Conference. Malaysia, Selangor.
- 3- Muneer M. Ba-abbad, Abdul Amir H. Kadhum, Abu bakar Mohamad Mohd S., Takriff, Kamaruzzaman Sopian. 2009. Solar photocatalytic degradation of 2, 4-dichlorophenol in water solution using ZnO catalyst. Proceeding of Environmental Science and Technology Conference (ESTEC2009) , Malaysia, Kuala Terengganu, pp.73-79.
- 4- Muneer M. Ba-abbad, Abdul Amir H. Kadhum, Abu bakar Mohamad Mohd S., Takriff, Kamaruzzaman Sopian. 2009. Titanium dioxide thin film as solar photocatalyst for a chlorinated degradation of organic contaminate. proceeding of the first international seminar on science and technology. Indonesia, pp.80.
- 5- Muneer M. Ba-abbad, Abdul Amir H. Kadhum, Abu bakar Mohamad, Mohd S., Takriff, Kamaruzzaman, 2010. Solar Photocatalytic Degradation of Environmental Pollutants Using ZnO Prepared by Sol-Gel: 2, 4-Dichlorophenol as Case Study. Proceeding of International Engineering Conference on hot arid regions (IECHAR2010), Al-Ahas, KSA, 175-179.
- 6- Muneer M. Ba-abbad, Abdul Amir H. Kadhum, Abu bakar Mohamad Mohd S., Takriff, Kamaruzzaman Sopian, Salmin S. Al-Shamali. 2010. Solar photocatalytic degrdation of aromatic chlorinated compound using titanium dioxide nanoparticles prepared by sol-gel method. Proceeding of 1st Annual

International Conference - Ibb 2010 'Environmental Science & Technology, Ibb city, Yemen, pp.33.

- 7- Muneer M. Ba-abbad, Abdul Amir H. Kadhum, Abu bakar Mohamad Mohd S., Takriff, Kamaruzzaman Sopian, Salmin S. Al-Shamali.2010. Solar photocatalytic degradation of aromaticchlorinated compound using zinc oxide nanoparticles prepared by sol-gel method.proceeding of the International Conference on Environment 2010 (ICENV 2010). Malaysia. Penang,pp.70.

C. List of selected papers

- 1- Muneer M. Ba-abbad, Abdul Amir H. Kadhum, Abu bakar Mohamad, Mohd S., Takriff, Kamaruzzaman,2010. Solar Photocatalytic Degradation of Environmental Pollutants Using ZnO Prepared by Sol-Gel: 2, 4-Dichlorophenol as Case Study. Int. J. of Thermal & Environmental Engineering, 1:37-42. Selected from International Engineering Conference on hot arid regions (IECHAR2010), Al-Ahas, KSA.
- 2- Muneer M. Ba-abbad, Abdul Amir H. Kadhum, Abu bakar Mohamad, Mohd S., Takriff, Kamaruzzaman, Visible light photocatalytic activity of Fe³⁺-doped ZnO nanoparticles prepared via sol-gel technique Chemosphere, 91(2013) 1604-1611.Selected as the one of top 25 article most download in Chemosphere journal within from April to July 2013 (article No.15), URL:
<http://top25.sciencedirect.com/subject/environmental-science/13/journal/chemosphere/00456535/archive/46/>
- 3- Muneer M. Ba-abbad, Abdul Amir H. Kadhum, Abu bakar Mohamad, Mohd S., Takriff, Kamaruzzaman, Visible light photocatalytic activity of Fe³⁺-doped ZnO nanoparticles prepared via sol-gel technique Chemosphere, 91(2013) 1604-1611.Selected as the one of top 25 article most download in Chemosphere journal within from July to September 2013 (article No.22), URL:
<http://top25.sciencedirect.com/subject/environmental-science/13/journal/chemosphere/00456535/archive/47/>



APPENDIX B

CHEMICAL, SOLVENT AND DEGRADANTS PROPERTIES

Table A-1 Specification of chemicals and solvents properties

No.	Name of chemical	Formula	Molecular weight(g/mol)	Purity (%)	Density gm/cm ³	Company
1-	Zinc acetate	ZnC ₄ H ₆ O ₄ .2H ₂ O	219.49	99.5	1.735	Merck
3-	Oxalic acid	C ₂ H ₂ O ₄ . 2H ₂ O	126.07	99.5	1.653	R &M Chemicals
4-	Iron(III) nitrate	Fe(NO ₃) ₃ .9H ₂ O	404.00	99.0	1.68	BDH Prolabo chemicals
5-	Iron(II) acetate	Fe(CH ₃ COO) ₂	173.93	95.0		Sigma-Aldrich
6-	Cobalt(II) acetate	Co(CH ₃ COO) ₂ .4H ₂ O	249.08	99.0		R &M Chemicals
7-	samarium(III) nitrate	Sm(NO ₃) ₃ · 6H ₂ O	444.47	99.9	2.375	Sigma-Aldrich
8-	Copper (II) acetate	Cu(CH ₃ COO) ₂ . H ₂ O	199.65	≥98%	1.882	Sigma-Aldrich
9-	Nickel (II) nitrate	Ni (NO ₃) ₂ . 6H ₂ O	290.81	97	2.05	Scharau
10-	Titanium (IV)	C ₁₂ H ₂₈ O ₄ Ti	284.215	97%	0.96	Sigma-Aldrich
11-	Ethanol Absolute	C ₂ H ₆ O	46.07	99.8		R &M Chemicals

Continue...

...Continued

12-	Hydrochloric Acid	HCl		37		Merck
13-	Sodium hydroxide	NaOH	39.9971	99.5	2.13	Merck
14-	Ammonia	NH ₃	17	28-30		J.T. Baker
15-	Hexane	C ₆ H ₁₄	86.18	96.0	0.66	Merck
16-	Ultra pure water	H ₂ O	18			
17-	Aceticacid anhydrous	C ₂ H ₄ O ₂	60.05	99.8	1.05	Merck
18-	Nitric acid	HNO ₃	63.01	65	1.5129	R &M Chemicals
19-	Nutrient agar					Oxoid Company
20-	Nutrient broth					Oxoid Company

Table A-2 Pollutants and color compounds properties

No.	Name of chemical	Formula	Molecular weight (g/mol)	Purity %	Density gm/cm ³ at 20°C	company
1-	2-chlorophenol	C ₆ H ₅ ClO	128.56	98	1.2634	Merck
2-	2,4-dichlorophenol	C ₆ H ₄ Cl ₂ O	163.00	97	1.38	Sigma-Aldrich
3-	2,4,6-trichlorophenol	C ₆ H ₃ Cl ₃ O	197.45	98	1.675	Supelco
4-	Methylene blue	C ₁₆ H ₁₈ N ₃ SCl	319.85		1.757	R&M Chemicals
5-	Methyl orange	C ₁₄ H ₁₄ N ₃ NaO ₃ S	327.33		1.28	R&M Chemicals
6-	Methyl Red	C ₁₅ H ₁₅ N ₃ O ₂	269.3		0.791	R&M Chemicals
7-	Lignin pink	C ₉ H ₁₀ O ₂ , C ₁₀ H ₁₂ O ₃ , C ₁₁ H ₁₄ O ₄				

APPENDIX C

STANADARD OF CHLOROPHENOLS

A. Specification of HPLC Colum

JONESCHROMATOGRAPHY

a world apart in separation

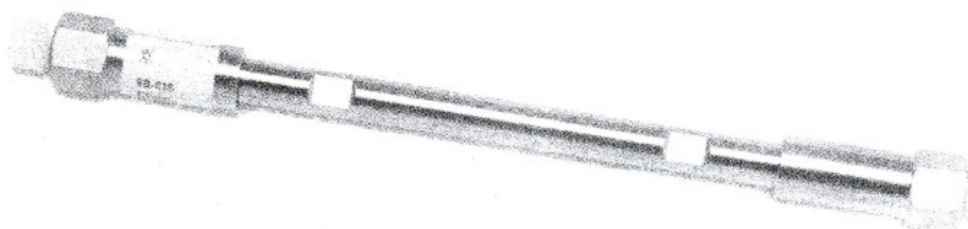
An **Argonaut** Technologies Company

COLUMN DETAILS

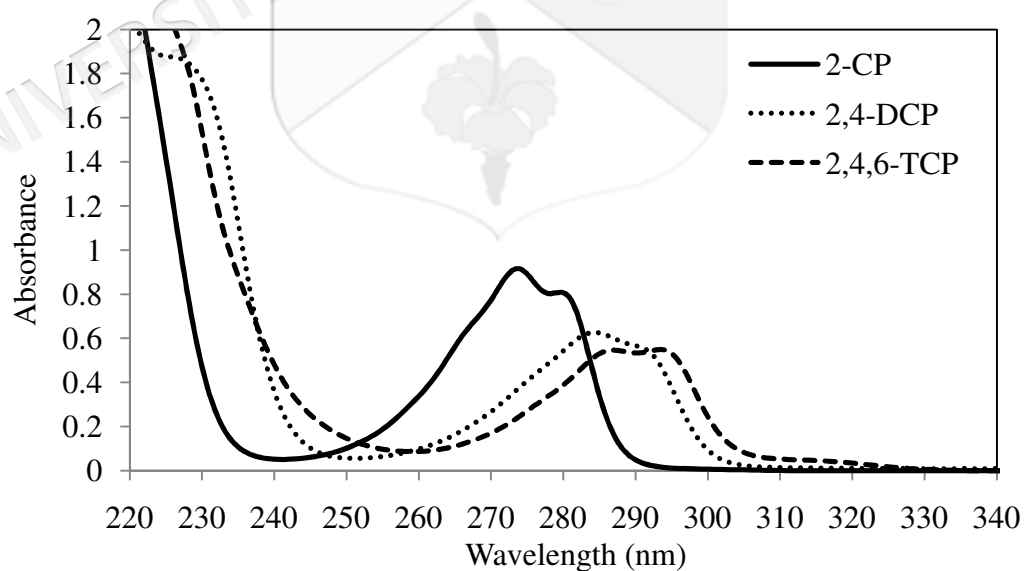
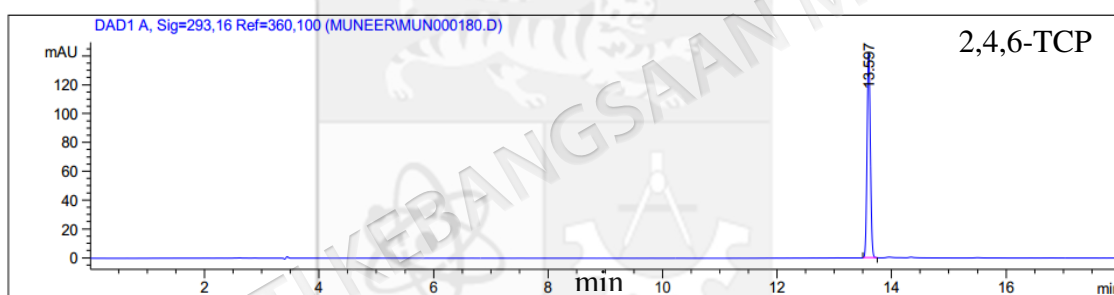
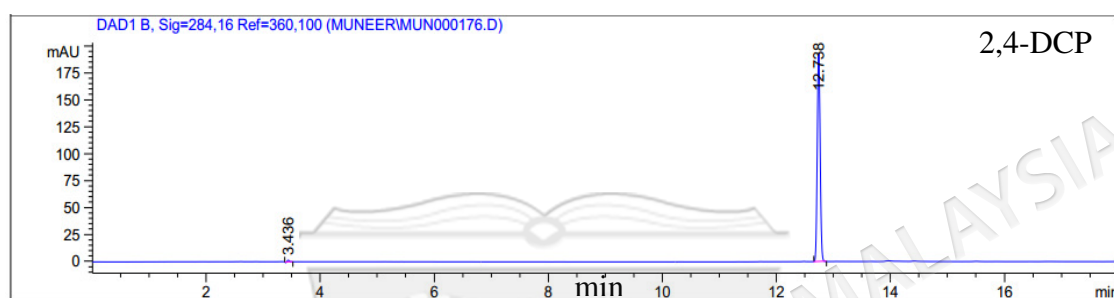
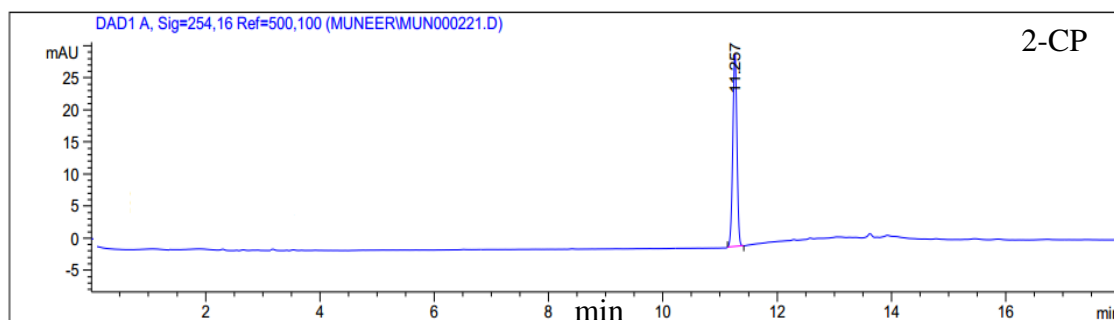
MATERIAL	: GENESIS C18 120A
	: 4u
CATALOGUE NUMBER	: FM25960E
SERIAL NUMBER	: 2121203
BATCH NUMBER	: 9600203
LENGTH (cm)	: 25
INSIDE DIAMETER (mm)	: 4.6
OUTSIDE DIAMETER (inch)	: 1/4
SHIP/STORE SOLVENT	: MOBILE PHASE

TEST CONDITIONS

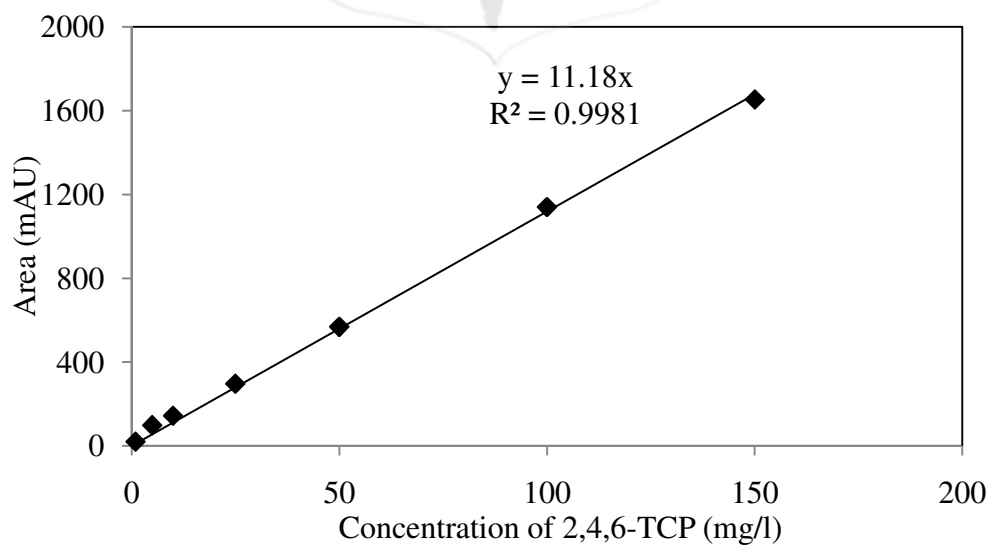
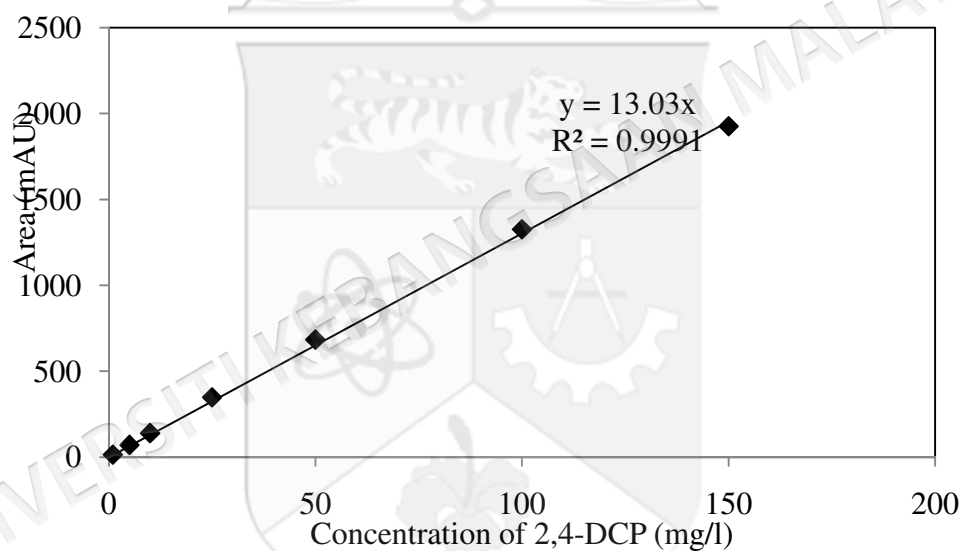
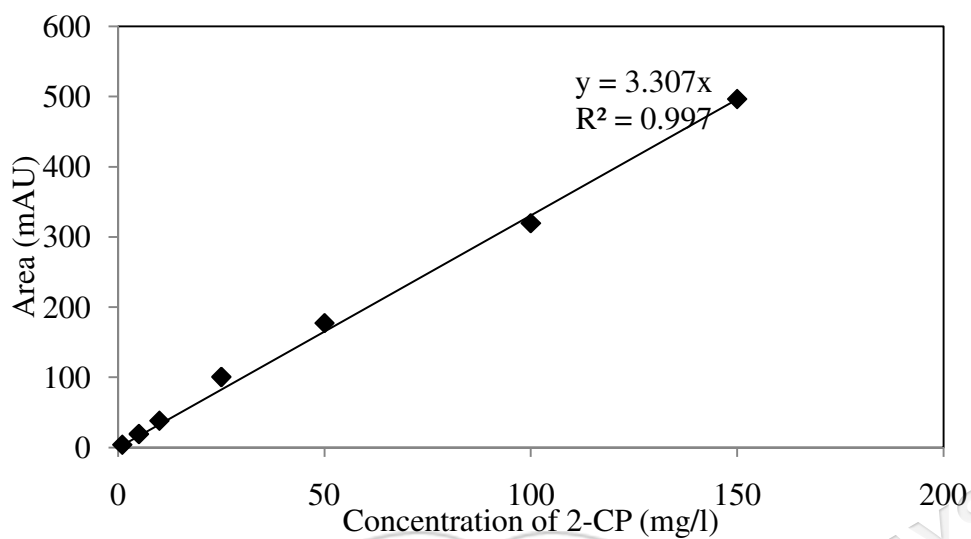
TEMPERATURE (Centigrade)	: 23
FLOW RATE (ml/min)	: 1.0
PRESSURE (bar)	: 68
LINEAR VELOCITY (cm/sec)	: 0.00
SAMPLE VOLUME (ul)	: 1
WAVELENGTH (nm)	: 254
MOBILE PHASE	: 75%MECN/H2O



B. Retention time of chlorophenols by HPLC



C. Standard of chlorophenols



APPENDIX E

SOLAR INTENSITY INSTRUMENT

A. UVA sensor



LIGHT

Ultra-violet A Sensor

- Climatology, meteorology
- UV effects on ecosystems
- Marine biology, ecology, zoology
- Studies of plant and animal responses to rising UV levels
- To monitor exposure of test samples in natural and other UV sources



Skye offer sensors to measure light levels in the Ultraviolet A and Ultraviolet B wavebands. The wavelengths used in these sensors are according to DIN 5031 part 7. This leaflet describes the UVA sensor.

The dimensions and overall look of these sensors are similar to that of our other

sensors. The housing is black aluminium and sealed to IP68 standards, making them suitable for underwater use. Skye guarantees sensors to a depth of 4 metres.

The light collecting head utilises a UV stable polymer and is cosine corrected.

The sensors have been

designed with an integral amplifier to give a voltage output for use with most dataloggers, computers, PLCs, etc.

All sensors are calibrated against a reference light source which is directly traceable to NPL and each sensor is issued with a calibration certificate.

Skye

B. UVB sensor



LIGHT

Ultra-violet B Sensor

- Climatology, meteorology
- UV effects on ecosystems
- Marine biology, ecology, zoology
- Studies of plant and animal responses to rising UV levels
- To monitor exposure of test samples in natural and other UV sources



Skye offer sensors to measure light levels in the Ultraviolet A and Ultraviolet B wavebands. The wavelengths used in these sensors are according to DIN 5031 part 7. This leaflet describes the UVB sensor.

The dimensions and overall look of these sensors are similar to that of our other

sensors. The housing is black aluminium and sealed to IP68 standards, making them suitable for underwater use. Skye guarantees sensors to a depth of 4 metres.

The light collecting head utilises a UV stable polymer and is cosine corrected.

The sensors have been

designed with an integral amplifier to give a voltage output for use with most dataloggers, computers, PLCs, etc.

All sensors are calibrated against a reference light source which is directly traceable to NPL and each sensor is issued with a calibration certificate.



C. Data logger



DATALOGGERS

DataHog2

-  Dedicated, accurate and reliable systems, which are easy to use, completely weatherproof, robust, durable and low cost
-  User selectable logging and integration intervals, plus a 24 hour summary
-  Multi-channel with a choice of voltage, current or digital count inputs
-  Optional electrical relay outputs for switching or alarm facilities
-  Battery operated with a choice of additional power supplies - solar and mains
-  Available with integral RH &/or Air Temperature sensors
-  Optional SkyeLynx Software Packages
-  Access via a portable PC, permanent cable link or GSM mobile phone remote data link
-  Real-time clock for synchronization with other installations



Applications

Environmental Monitoring
 Weather Stations
 Process Monitoring
 Energy Management
 Agricultural Research
 Product Storage
 Transportation of Sensitive Goods
 Museums and Art Galleries
 Environmental Audits
 Pollution Studies
 Emission Monitoring
 Landfill Sites
 Environmental Chambers
 Cold Chain use
 Horticulture

The Skye DataHog loggers have been available for several years as small easy to use devices suitable for many applications.

The DataHog2 has a large storage memory and extended battery life to allow long term projects to be monitored at remote sites, or short term logging at frequent intervals. The range of input types is varied - customers can use their own sensors or choose from Skye's range of precision sensors. Choose combinations of single ended or differential voltage, current inputs or digital count.

Channels can be individually programmed with logging interval and gain to suit each sensor type. Units for scaling are defined by the user for easy and straightforward operation. At user-set levels, the DataHog2 will give an electrical relay or alarm output from up to two different channels. There is also a timed start/stop function.

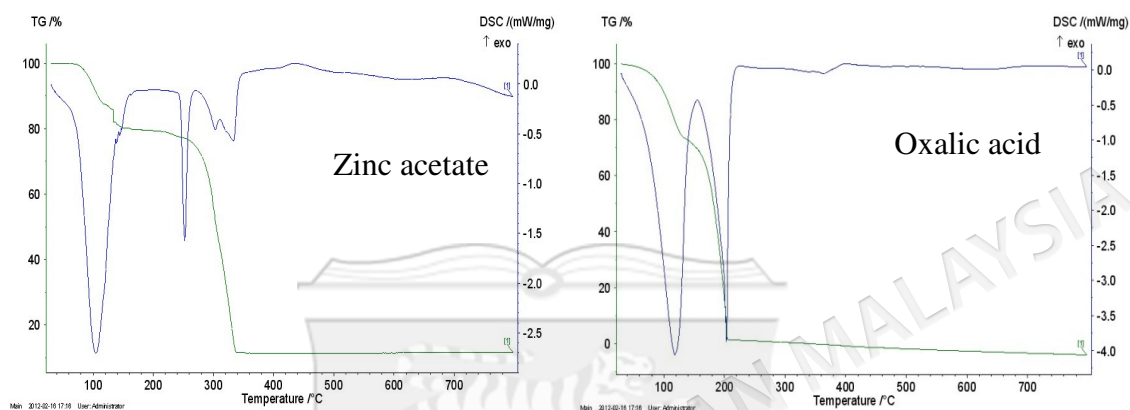
Supplied with a 'ready-to-go' package of batteries, datalead & Windows communication software



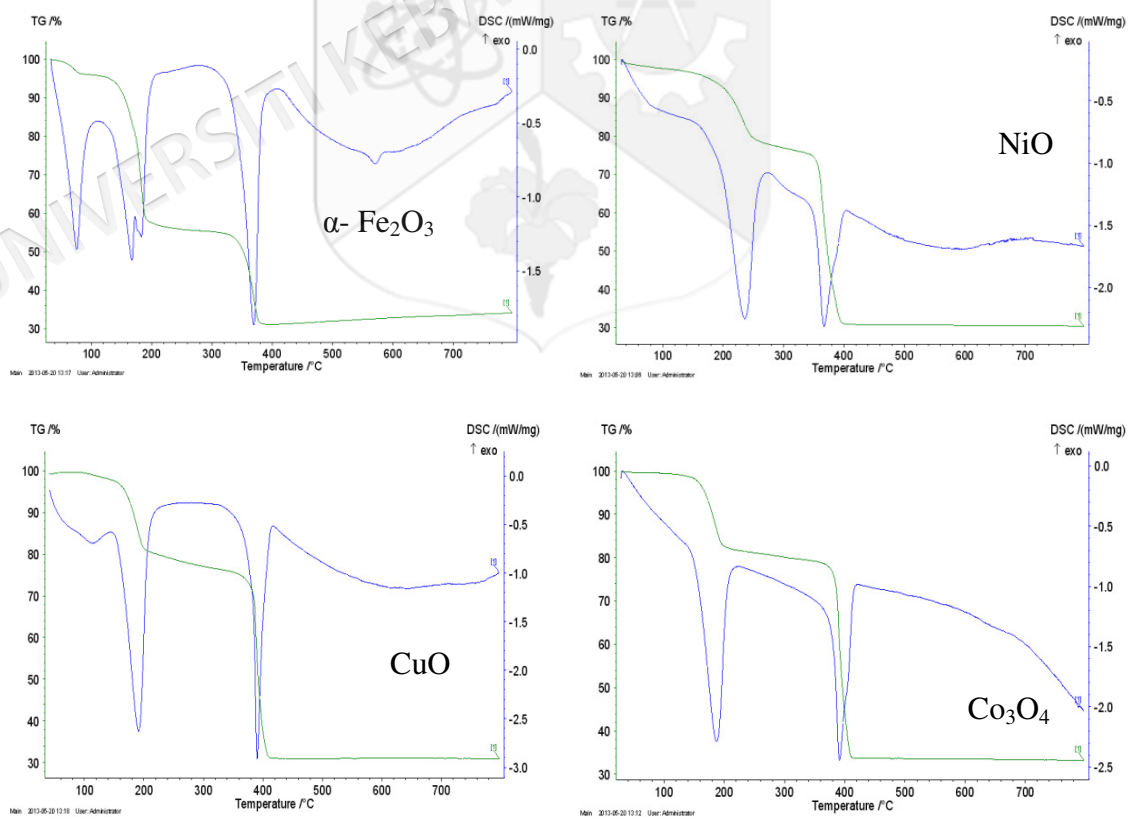
APPENDIX F

TGA-DSC ANALYSIS

A. Precursor material



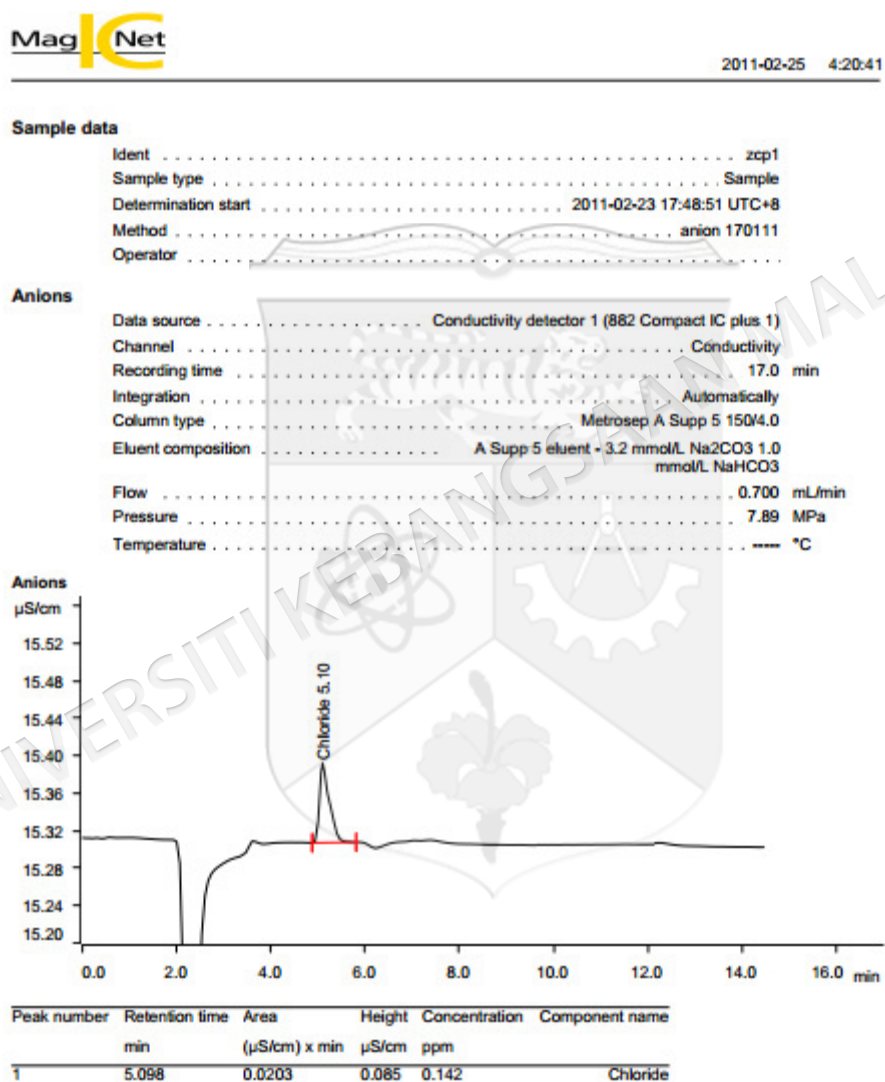
B. Other metal oxide



APPENDIX G

CHLORIDE IONS CONCENTRATION (Cl^-)

A. 2-CP



B. 2,4-DCP

MagNet

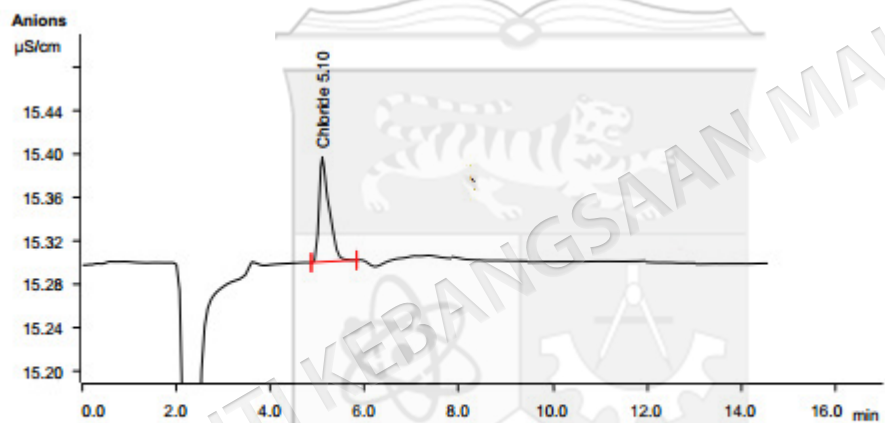
2011-02-25 4:20:55

Sample data

Ident zcp2
 Sample type Sample
 Determination start 2011-02-23 18:10:14 UTC+8
 Method anion 170111
 Operator

Anions

Data source Conductivity detector 1 (882 Compact IC plus 1)
 Channel Conductivity
 Recording time 17.0 min
 Integration Automatically
 Column type Metrosep A Supp 5 150/4.0
 Eluent composition A Supp 5 eluent + 3.2 mmol/L Na₂CO₃ 1.0 mmol/L NaHCO₃
 Flow 0.700 mL/min
 Pressure 7.89 MPa
 Temperature °C



Peak number	Retention time	Area	Height	Concentration	Component name
	min	(μS/cm) x min	μS/cm	ppm	
1	5.098	0.0234	0.096	0.179	Chloride

C. 2,4,6-TCP

MagNet

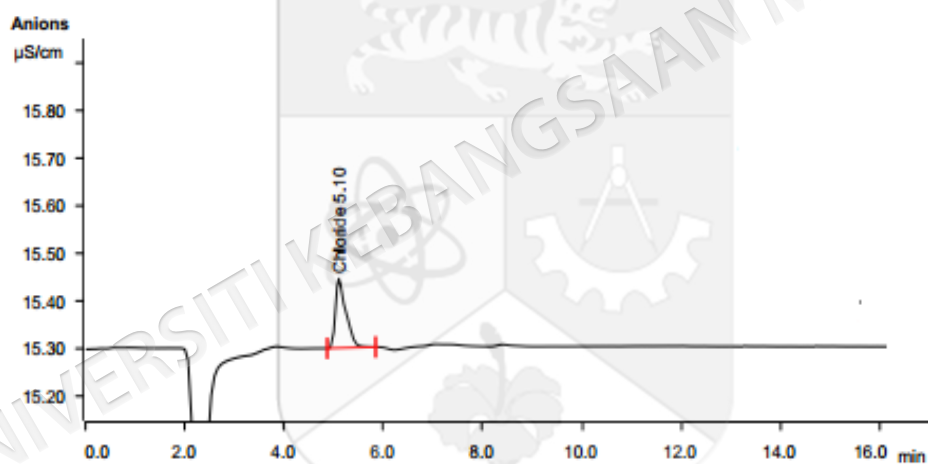
2011-02-25 4:21:36

Sample data

Ident
 Sample type Sample
 Determination start 2011-02-23 19:14:26 UTC+8
 Method anion 170111
 Operator

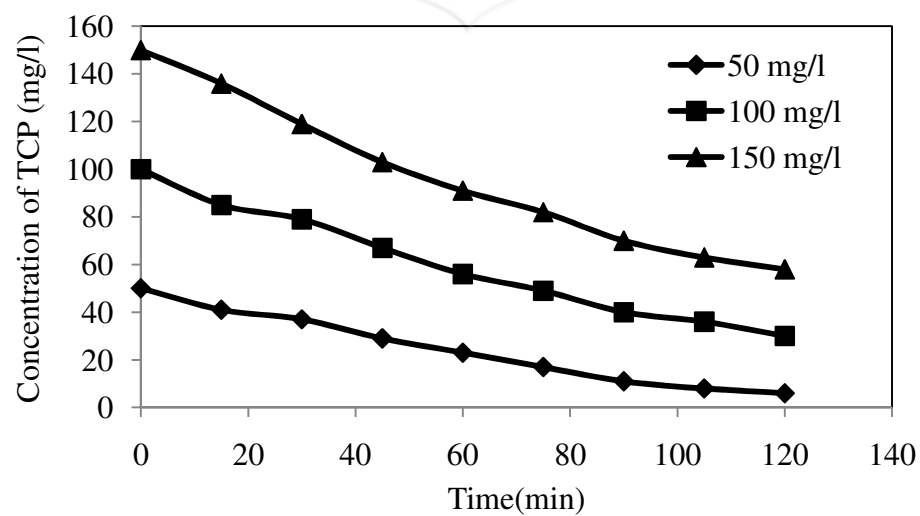
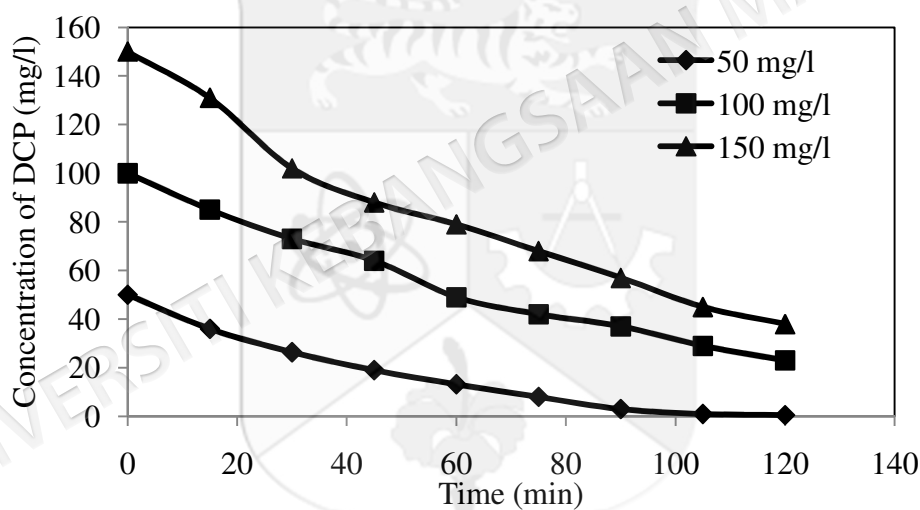
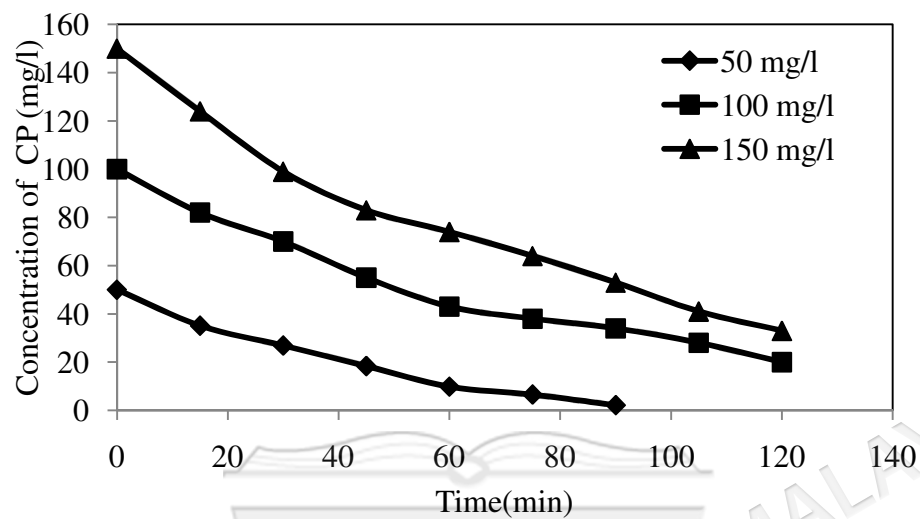
Anions

Data source Conductivity detector 1 (882 Compact IC plus 1)
 Channel Conductivity
 Recording time 17.0 min
 Integration Automatically
 Column type Metrosep A Supp 5 150/4.0
 Eluent composition A Supp 5 eluent - 3.2 mmol/L Na₂CO₃ 1.0 mmol/L NaHCO₃
 Flow 0.700 mL/min
 Pressure 7.89 MPa
 Temperature °C



Peak number	Retention time	Area	Height	Concentration	Component name
	min	(μS/cm) x min	μS/cm	ppm	
1	5.102	0.0353	0.146	0.327	Chloride

APPENDIX H

DEGRADATION OF CHLOROPHENOLS USING Sm^{3+} and Ti^{4+} DOPED ZNO

APPENDIX I

ATOMIC ABSORPTION SPECTROSCOPY ANALYSIS

A. Pure of ZnO

Sample No.1

Repl #	SampleConc mg/L	StndConc mg/L	BlkCorr Signal	Time	Signal Stored
1	8.684	8.684	1.190	15:08:25	No
	Sample concentration is greater than that of the highest standard.				
2	8.762	8.762	1.195	15:08:32	No
	Sample concentration is greater than that of the highest standard.				
3	8.840	8.840	1.201	15:08:39	No
	Sample concentration is greater than that of the highest standard.				
Mean:	8.762	8.762	1.195		
SD:	0.078	0.078	0.0057		
%RSD:	0.888	0.888	0.48		
	Sample concentration is greater than that of the highest standard.				

Sample No.2

Repl #	SampleConc mg/L	StndConc mg/L	BlkCorr Signal	Time	Signal Stored
1	8.759	8.759	1.358	13:33:14	No
	Sample concentration is greater than that of the highest standard.				
2	8.903	8.903	1.362	13:33:21	No
	Sample concentration is greater than that of the highest standard.				
3	9.418	9.418	1.375	13:33:28	No
	Sample concentration is greater than that of the highest standard.				
Mean:	9.027	9.027	1.365		
SD:	0.346	0.346	0.0088		
%RSD:	3.833	3.833	0.65		

Sample No.3

Repl #	SampleConc mg/L	StndConc mg/L	BlkCorr Signal	Time	Signal Stored
1	8.759	8.759	1.358	13:33:14	No
	Sample concentration is greater than that of the highest standard.				
2	8.903	8.903	1.362	13:33:21	No
	Sample concentration is greater than that of the highest standard.				
3	9.418	9.418	1.375	13:33:28	No
	Sample concentration is greater than that of the highest standard.				
Mean:	9.027	9.027	1.365		
SD:	0.346	0.346	0.0088		
%RSD:	3.833	3.833	0.65		

Sample No.4

Repl #	SampleConc mg/L	StdConc mg/L	Blncorr Signal	Time	Signal Stored
1	9.021	9.021	1.381	12:59:41	No
Sample concentration is greater than that of the highest standard.					
2			1.573	12:59:50	No
Sample absorbance is beyond the range of the calibration function.					
3	9.777	9.777	1.399	12:59:58	No
Sample concentration is greater than that of the highest standard.					
Mean:	9.399	9.399	1.451		
SD:	0.535	0.535	0.1057		
%RSD:	5.688	5.688	7.29		

B. Fe³⁺ doped ZnO

Sample No.1

Repl #	SampleConc mg/L	StdConc mg/L	Blncorr Signal	Time	Signal Stored
1	4.497	4.497	0.750	15:11:44	No
2	4.604	4.604	0.765	15:11:50	No
3	4.647	4.647	0.771	15:11:57	No
Mean:	4.583	4.583	0.762		
SD:	0.078	0.078	0.0106		
%RSD:	1.691	1.691	1.39		

Sample No.2

Repl #	SampleConc mg/L	StdConc mg/L	Blncorr Signal	Time	Signal Stored
1	2.395	2.395	0.728	13:15:53	No
2	2.187	2.187	0.676	13:16:00	No
3	2.120	2.120	0.658	13:16:07	No
Mean:	2.234	2.234	0.687		
SD:	0.143	0.143	0.0364		
%RSD:	6.411	6.411	5.29		

C. Fe³⁺ ions

Sample No.1

Repl #	SampleConc mg/L	StdConc mg/L	Blncorr Signal	Time	Signal Stored
1	-0.004	-0.004	-0.000	13:31:37	No
2	0.012	0.012	0.001	13:31:42	No
3	-0.004	-0.004	-0.000	13:31:47	No
Mean:	0.001	0.001	0.000		

Sample No.2

Repl #	SampleConc mg/L	StdConc mg/L	Blncorr Signal	Time	Signal Stored
1	-0.007	-0.007	-0.001	13:33:17	No
2	-0.012	-0.012	-0.001	13:33:22	No
3	0.000	0.000	-0.000	13:33:27	No
Mean:	-0.006	-0.006	-0.001		
SD:	0.006	0.006	0.0005		
%RSD:	94.20	94.20	94.20		

APPENDIX J

DETERMINATION OF INTERMEDIATE COMPOUNDS

A. Spaecification of GC-MS colum

GC and GC/MS Applications/ Industrial Chemicals

Phenols

Column: HP 5MS

30 m x 0.25 mm ID, 0.25 μ m

P/N: 19091-5433

Carrier: Helium, 33 cm/sec, constant flow

Oven: 35°C for 5 min

35-220°C at 8°C/min

Injection: 1 μ L, Splitless, 250°CSample: 20 μ g/mL phenols in methylene chloride

Purge Time: 0.75 min

Detector: FID 300°C

1. Phenol
2. 2-Chlorophenol
3. 2-Nitrophenol
4. 2,4-Dimethylphenol
5. 2,4-Dichlorophenol
6. 4-Chloro-3-methylphenol
7. 2,4,6-Trinitrophenol
8. 2,4-Dinitrophenol
9. 4-Nitrophenol
10. 2-Methyl-4,6-dinitrophenol
11. Pentachlorophenol

Suggested Supplies:

Liner:

Single Taper, Direct Connect,
deactivated, G1544-80730

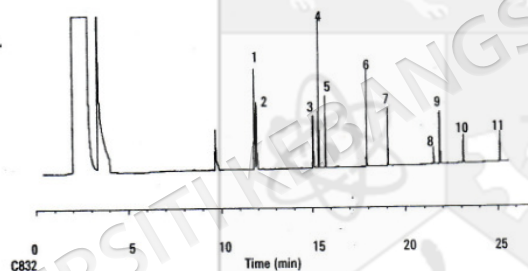
Septum:

Advanced Green, 5183-4759

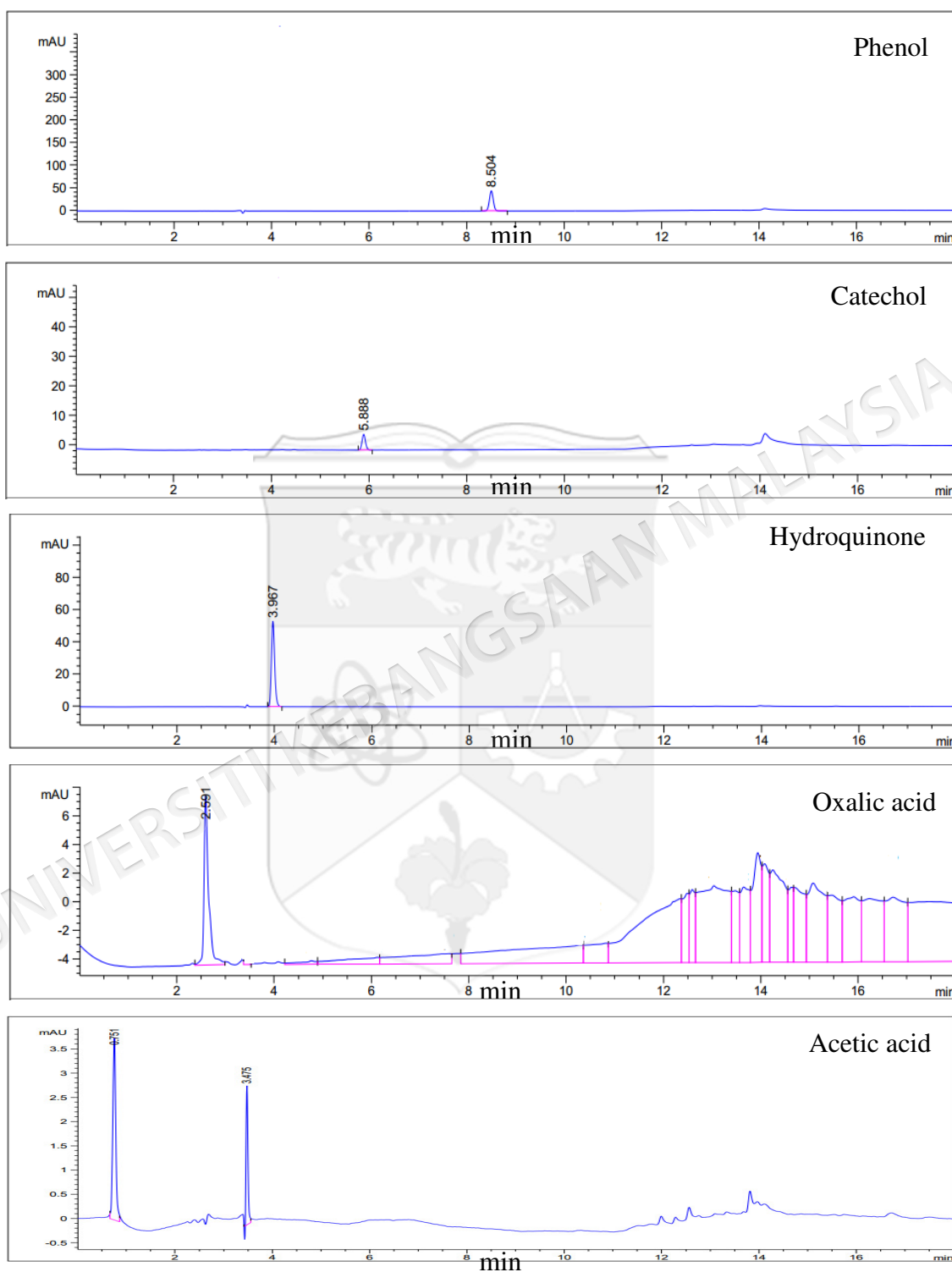
Seal:

Gold-plated, 18740-20885

Syringe:

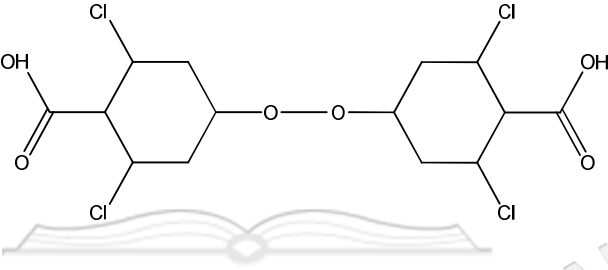
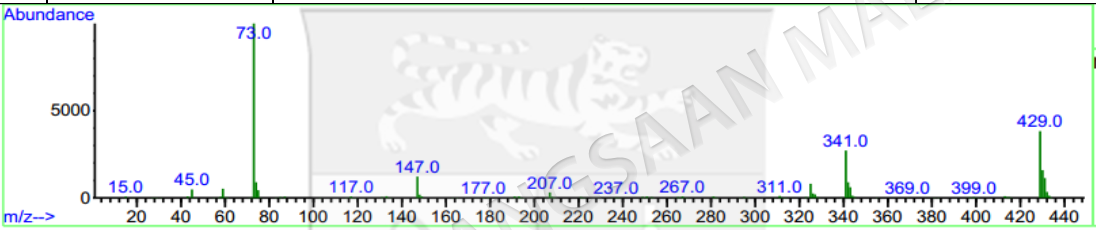
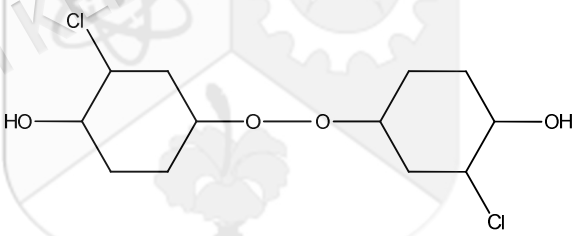
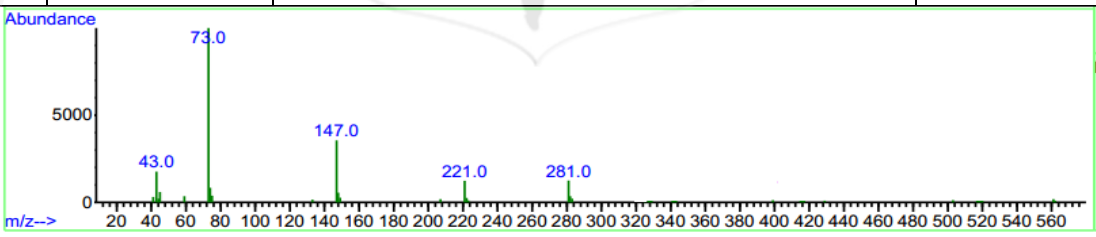
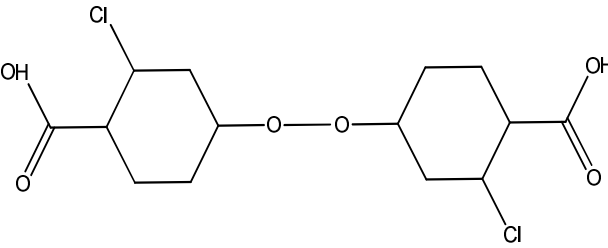
10 μ L, 23-26s/42/HP, Tapered, fixed
5181-1267

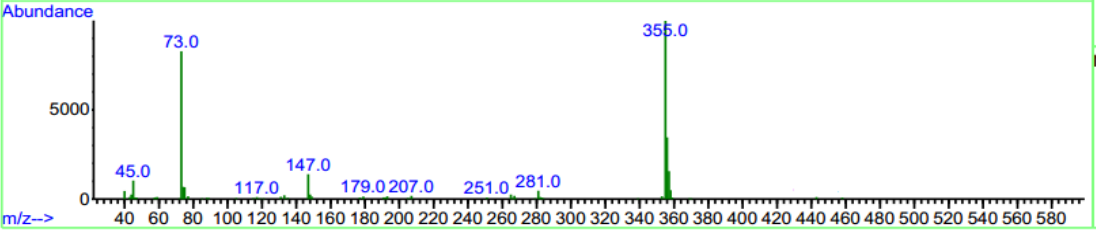
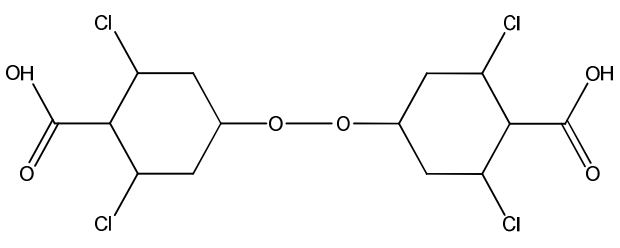
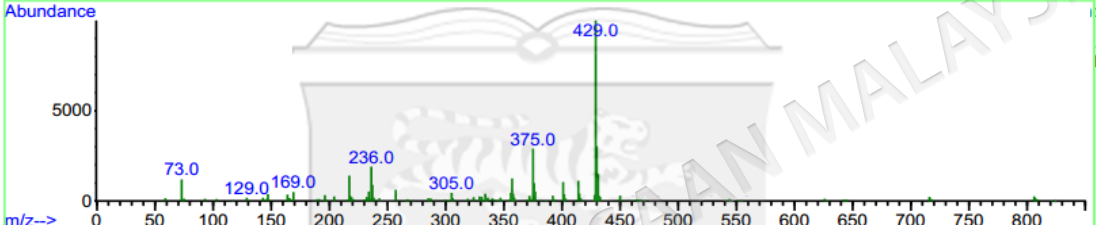
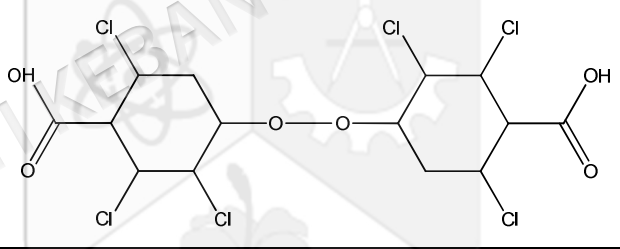
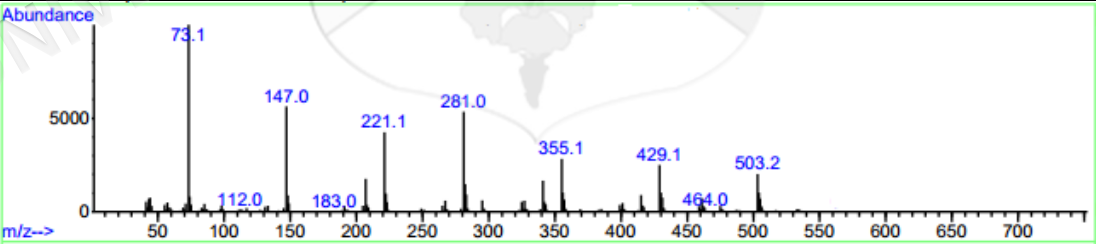
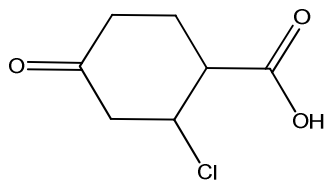
B. Intermediates compound using HPLC

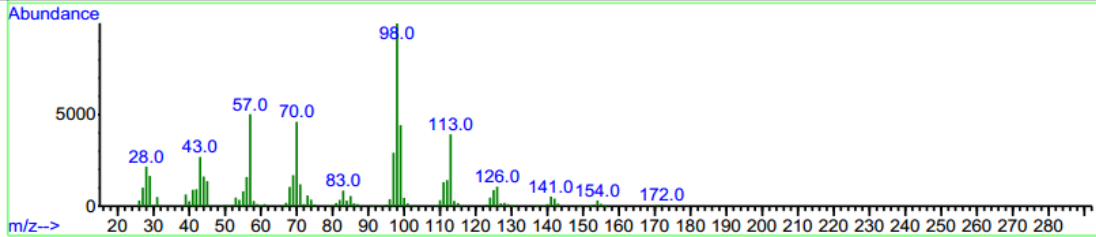
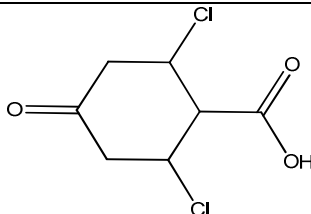
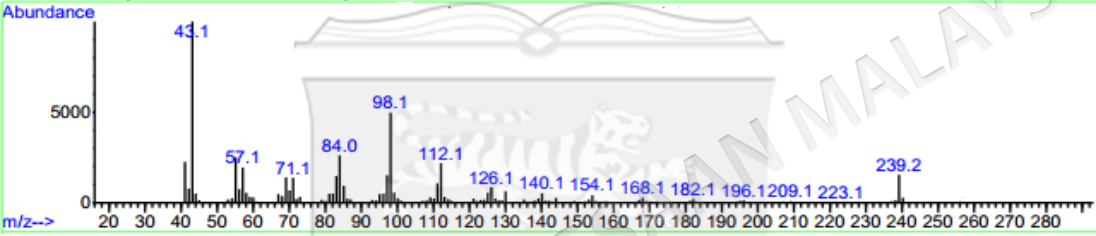
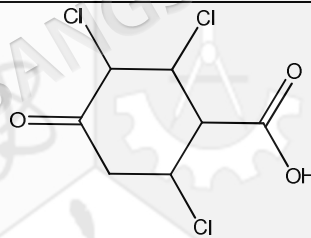


APPENDIX K

STRUCTURE AND MOLECULAR WEIGHT OF INTERMEDIATES USING
GC-MS

N o	Retention Time (min)	Molecular structure of compound	Molecular weight(Mwt)
1	6.30		429 2-CP 2,4-DCP 2,4,6-TCP
			
2	7.43		288 2-CP 2,4-DCP 2,4,6-TCP
			
3	8.44		355 2-CP 2,4-DCP 2,4,6-TCP

			
4	9.31		429 2-CP 2,4-DCP 2,4,6-TCP
			
5	10.09		503 2,4,6-TCP
			
6	10.70	 2-chloro-4-oxocyclohexanecarboxylic acid	176 2-CP

			
7	10.70	 2,6-dichloro-4-oxocyclohexanecarboxylic acid Molecular Weight: 211.04	211 2,4-DCP
			
8	10.70	 2,3,6-trichloro-4-oxocyclohexanecarboxylic acid Molecular Weight: 245.49	246 2,4,6-TCP
