



UNIVERSITI PUTRA MALAYSIA

**PHOTODEGRADATION-ADSORPTION OF ORGANIC DYES USING
IMMOBILIZED CHITOSAN SUPPORTED TITANIUM DIOXIDE
PHOTOCATALYST**

LEE KONG HUI

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ORGANIC DYES USING IMMOBILIZED
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PHOTOCATALYST**

LEE KONG HUI

**DOCTOR OF PHILOSOPHY
UNIVERSITI PUTRA MALAYSIA**

2007



**PHOTODEGRADATION-ADSORPTION OF ORGANIC DYES USING
IMMOBILIZED CHITOSAN SUPPORTED TITANIUM DIOXIDE
PHOTOCATALYST**

By

LEE KONG HUI

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia,
in Fulfilment of the Requirement for the degree of Doctor of Philosophy**

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TABLE OF CONTENTS

	Page
DEDICATION	ii
ABSTRACT	iii
ABSTRAK	vi
ACKNOWLEDGEMENTS	ix
APPROVAL	xi
DECLARATION	xiii
LIST OF TABLES	xvii
LIST OF FIGURES	xix
LIST OF ABBREVIATIONS/NOTATIONS/GLOSSARY OF TERMS	xxviii

CHAPTER

1	INTRODUCTION	1
	1.1 Theory of Semiconductor	5
	1.2 Properties of TiO ₂ as Semiconductor	8
	1.2.1 Structural properties	9
	1.2.2 Optical properties	13
	1.2.3 Electrical properties	15
	1.3 Photodegradation on Semiconductor	17
	1.3.1 Electrons and holes	17
	1.4 Role of Oxygen	19
	1.5 Properties of Chitosan	22
	1.5.1 Adsorption properties	23
	1.5.2 Adhesion properties	24
	1.6 Glass as Support for TiO ₂ -Chitosan	24
	1.8 Properties of Dyes	27
	1.9 Objectives	31
2	LITERATURE REVIEW	33
	2.1 Effect of TiO ₂ in the Treatment of Pollutants	33
	2.2 Kinetics Studies on Photocatalytic Degradation	34
	2.3 Utilization of Light Irradiation for TiO ₂ Particles Excitation	35
	2.4 Effect of Adsorbent as a Support for TiO ₂ Photocatalysts	38
	2.5 Application of TiO ₂ Thin Film in Enhancing the Photodegradation Efficiency	39
	2.6 Chitosan as an Adsorbent	40
	2.7 Effect of Using Co-adsorbent in Photodegradation Process	41



3	MATERIALS AND METHODOLOGY	43
	3.1 Precursor Materials Used in the Preparation of Titanium Dioxide Slurry	43
	3.2 Preparation of Titanium Dioxide Slurry in Chitosan	44
	3.3 Preparation of Titanium Dioxide Coated on Glass (TiO ₂ -Chitosan/Glass)	44
	3.4 TiO ₂ -Chitosan/Glass Characterization	46
	3.4.1 Scanning Electron Microscope fitted with energy dispersive X-ray Spectrometer (SEM-EDX) analysis	46
	3.4.2 X-ray diffraction (XRD) analysis	47
	3.4.3 Fourier Transform-Infrared (FT-IR) Analysis	49
	3.4.4 Surface Area and Porosity Analysis (ASAP)	50
	3.4.5 Thermal Property Analysis (Thermogravimetric / Scanning Differential Thermogravimetric Analysis – TG/SDTA)	51
	3.5 Preparation of Dyes Solution	52
	3.6 Determination of Wavelength at Maximum Absorption (λ_{\max}) and Construction of Standard Calibration Curve for Dyes	53
	3.7 Analysis of Intermediates	54
	3.7.1 Total Organic Carbon Analysis (TOC)	54
	3.7.2 Gas Chromatography-Mass Spectrometry (GC/MS) with Direct Insertion-Mass Spectrometry (DI/MS) analysis	56
	3.8 Photodegradation and Adsorption of Methyl Orange (An Anionic Dye of the Azo Series)	57
	3.8.1 Effect of TiO ₂ : Chitosan ratio	57
	3.8.2 Effect of photocatalyst loading (Sol dip-coating repetition)	59
	3.8.3 Effect of different initial concentration	59
	3.8.4 Effect of light intensity	60
	3.8.5 Effect of using different light source	61
	3.8.6 Effect of solution temperature	62
	3.8.7 Effect of solution pH	62
	3.9 Photodegradation and Adsorption of Methylene Blue, MB (a Cationic dye)	64
	3.10 Photodegradation and Adsorption of Mixed Dye, MD (a mixture of MO and MB)	64
	3.11 Photodegradation and adsorption of Model Pollutants Applying Optimum Experimental Condition	65
4	RESULTS AND DISCUSSION	66
	4.1 Surface Morphology of TiO ₂ -Chitosan Coated on Glass photocatalyst (TiO ₂ -Chitosan/Glass)	66
	4.2 XRD Characterization of TiO ₂ Compound	71
	4.2.1 Crystallite phase determination of TiO ₂ compound	71
	4.2.2 Crystallite size of Anatase phase TiO ₂	74
	4.3 Fourier Transform-Infrared (FT-IR) Analysis for TiO ₂ , Chitosan, and TiO ₂ -Chitosan/Glass Photocatalyst	76
	4.4 Surface Area and Porosity Analysis (ASAP)	80

4.5 Thermal Property Analysis of the Precursor Materials and TiO ₂ -Chitosan Catalyst	84
4.6 Preliminary Tests and Control	89
4.6.1 Consistency of TiO ₂ -Chitosan catalyst loading	89
4.6.2 Adhesion stability of the coated TiO ₂ -Chitosan catalyst film	91
4.6.3 Determination of wavelength at maximum absorption (λ_{max}) and construction of standard calibration curve for dyes concentration detection	92
4.6.4 Preliminary test (control test)	97
4.7 Effect of TiO ₂ Degussa P 25 : Chitosan Ratio	98
4.8 Effect of TiO ₂ -Chitosan Catalyst Loading (Sol Dip-coating Repetition)	102
4.8.1 First order kinetics	108
4.8.2 Pseudo-second kinetics order	110
4.9 Effect of Different Initial Concentration	121
4.10 Effect of Light intensity	129
4.11 Effect of Using Different Light Source	135
4.12 Effect of Solution Temperature	141
4.13 Effect of Solution pH	150
4.14 Photodegradation and Adsorption of Methylene Blue (a Cationic dye)	162
4.15 Photodegradation of Mixed Dyes	172
4.16 Photodegradation of Model Pollutants Applying Optimum Experimental Condition	181
4.17 Qualitative Analysis and the Determination of Photodegradation-Adsorption Reactions Pathways	186
4.17.1 Total Organic Carbon (TOC) Analysis for MO	186
4.17.2 Total Organic Carbon (TOC) Analysis for MB	191
4.17.3 GC/MS with DI/MS Analysis for MO	194
4.17.4 GC/MS with DI/MS Analysis for MB	218
5 CONCLUSION AND RECOMMENDATION	237
5.1 Conclusion	237
5.2 Recommendation	239
BIBLIOGRAPHY	243
APPENDICES	253
BIODATA OF THE AUTHOR	277



LIST OF TABLES

Table	Page
1.1 Crystallographic properties of anatase, rutile and brookite (Wold, 1993)	10
1.2 Properties of Methylene Blue (Zollinger, 1987, 2003)	29
1.3 Properties of Methyl Orange (Zollinger, 1987, 2003)	30
4.1 Atomic mass ratio of titanium to oxygen of ca. 1:2 to the nearest moles ratio	70
4.2 Characteristics of BET surface area and average pore diameter adsorption of N ₂ (g) on the used precursor materials and dried catalysts with different TiO ₂ Degussa P 25 ratio	83
4.3 Amount of TiO ₂ -Chitosan catalyst coated on the glass plates with different dip-coating repetition	89
4.4 Standard deviation value and mean amount of TiO ₂ -Chitosan catalyst coated on the glass plates with different dip-coating repetition	90
4.5 Photodegradation-adsorption removal of MO applying different ratio of TiO ₂ : Chitosan (Concentration of dye = 20 ppm)	102
4.6 The apparent rate constant, k_{app} , half life, $t_{1/2}$, and removal efficiency values for the adsorption of MO with different dip-coating repetition	114
4.7 The apparent rate constant, k_{app} , half life, $t_{1/2}$, and removal efficiency values for the total removal of MO with different dip-coating repetition	115
4.8 The apparent rate constant, k_{app} , values for the photodegradation-adsorption of MO with different dip-coating repetition	119
4.9 The apparent rate constant, k_{app} , half life, $t_{1/2}$, and removal efficiency values for the adsorption of MO with different initial concentration	125
4.10 The apparent rate constant, k_{app} , half life, $t_{1/2}$, and removal efficiency values for the total / photodegradation removal of MO with different initial concentration	128
4.11 The apparent rate constant, k_{app} , half life, $t_{1/2}$, and removal efficiency values for the removal of MO applying different light intensity (Concentration of dye = 20 ppm)	129



4.12	The apparent rate constant, k_{app} , half life, $t_{1/2}$, and removal efficiency values for the removal of MO under different light source irradiation	139
4.13	Temperature dependence of apparent rate constant, k_{app} , half life, $t_{1/2}$, and removal efficiency values for the removal of MO due to adsorption process	148
4.14	Temperature dependence of apparent rate constant, k_{app} , half life, $t_{1/2}$, and removal efficiency values for the total / photodegradation removal of MO	148
4.15	pH dependence of apparent rate constant, k_{app} , correlation factor, R^2 , and removal efficiency values for the adsorption process of MO	154
4.16	pH dependence of apparent rate constant, k_{app} , correlation factor, R^2 , and removal efficiency values for the total / photodegradation removal of MO	160
4.17	pH dependence of apparent rate constant, k_{app} , half life, $t_{1/2}$, and removal efficiency values for the removal of MB due to adsorption process	165
4.18	pH dependence of apparent rate constant, k_{app} , half life, $t_{1/2}$, and removal efficiency values for the total / photodegradation removal of MB	169
4.19	pH dependence of MO and MB removal in mixed dyes due to adsorption process	180
4.20	pH dependence for the total / photodegradation removal of MO and MB in mixed dyes	180
4.21	Apparent rate constant, k_{app} , half life, $t_{1/2}$, and removal efficiency values for the removal of MO and MB under optimum condition (500 ml, 20 ppm)	185
4.22	Initial “parent molecule” of MO and its intermediate compounds identified from the DI/MS analysis at different interval times	196
4.23	Initial “parent molecule” of MB and its respective by-products identified from the DI/MS analysis at different interval times	219

LIST OF FIGURES

Figure	Page
1.1 The energy gap (E_g) difference between the metal, insulator and Semiconductor	5
1.2 The energy diagram for a semiconductor, showing the band gap energy (Nogueira and Wilson, 1993)	6
1.3 Change in the electronic structure of a semiconductor compound as the number N of monomeric units present increase from unity to clusters of more than 2000 (Mills and Hunte, 1997)	7
1.4 Structure of anatase TiO_2 , titanium dark, oxygen light (Shriver <i>et al.</i> , 1990)	11
1.5 Structure of rutile TiO_2 , titanium dark, oxygen light (Shriver <i>et al.</i> , 1990)	11
1.6 Formation of surface hydroxyls (OH) on the anatase TiO_2 surface (Shriver <i>et al.</i> , 1990)	12
a) An uncovered surface	
b) Coordination of Ti^{4+} ions by water molecules	
c) The formation of surface hydroxyl ions by proton transfer from water to O_2^- ions	
1.7 Band structure of (a) indirect transition (b) direct transition (Lewis and Rosenbluth, 1989; Shriver <i>et al.</i> , 1990)	15
1.8 Energy diagram for a dark and irradiated semiconductor (Atkins, 1995)	16
E^o = Fermi level	
pE_F^o = Quasi Fermi level for holes	
nE_F^o = Quasi Fermi level for electron	
1.9 Energy working scheme for a redox process (Shriver <i>et al.</i> , 1990)	16
1.10 Illustration of the major processes occurring on a semiconductor particle following electronic excitation (Mills and Hunte, 1997)	18
1.11 Schematic representation for deacetylation of chitin to produce chitosan (Yoshizuka <i>et al.</i> , 2000 and Prado <i>et al.</i> , 2004)	22
3.1 Scanning Electron Microscope - LEO 1455 VPSEM instrumental set-up for surface morphology analysis	46



3.2	Energy dispersive X-ray Spectrometer-Oxford INCA EDX instrumental set-up for samples compound quantification	47
3.3	XRD-6000 instrumental set-up for XRD analysis	48
3.4	Perkin Elmer Spectrum BX FT-IR instrumental set-up for chemical compound substituents and functional groups analysis	49
3.5	Micromeritics ASAP 2000 accelerated surface area and porosimetry system analytical instrument	50
3.6	Mettler Toledo TG/SDTA analytical instrument	51
3.7	Perkin Elmer Lambda 20 UV/Vis Spectrometer for wavelength at maximum absorption (λ_{max}) and samples concentration determination	54
3.8	SGE ANATOC Series II Total Organic Carbon Analyzer with ANATOC Series II Autoinjection System and ANATOC Autosampler machine	55
3.9	Shimadzu Lab Solutions GCMS-QP5050A with Shimadzu GC-17A Direct Insertion-Mass Spectrometry (DI/MS) single compound injection probe system	56
3.10	Experimental set-up of the photodegradation-adsorption process. (a) O ₂ and bubbling effect, (b) Quartz glass housing, (c) White fluorescent light source, (d) TiO ₂ -Chitosan/Glass photocatalyst, (e) Sampling outlet, (f) Reactor tank, and (g) Model pollutant (MO)	58
4.1	SEM micrographs of the raw material used to prepare TiO ₂ -Chitosan/Glass photocatalyst, X 20,000 (a) chitosan and (b) Degussa P 25 TiO ₂	66
4.2	SEM-EDX micrographs of TiO ₂ -Chitosan/Glass with different photocatalyst loading, X 20,000 (a) 1 layer, (b) 2 layers, (c) 3 layers, (d) 4 layers, (e) 5 layers, and (f) 4 layers/25.0 g of TiO ₂ Degussa P-25	68
4.3	The EDX analysis confirming atomic mass ratio of titanium to oxygen of ca. 1:2 for 4 dip-coated photocatalyst (2.5 g chitosan : 2.5 g TiO ₂ Degussa P-25)	69



4.4	X-ray diffraction patterns of TiO ₂ -Chitosan/Glass (2.5 g chitosan : 2.5 g TiO ₂ Degussa P 25) with different photocatalyst loading (1 to 6 dip-coating layers) dried at 100 °C	72
4.5	X-ray diffraction patterns of TiO ₂ -Chitosan/Glass (2.5 g chitosan : 25.0 g TiO ₂ Degussa P 25) with different photocatalyst loading (1 to 6 dip-coating layers) dried at 100 °C	73
4.6	Crystallite size of anatase TiO ₂ crystalline in 2.5 g chitosan : 2.5 g TiO ₂ Degussa P 25 photocatalyst with different photocatalyst loading (1 to 6 dip-coating layers)	74
4.7	Crystallite size of anatase TiO ₂ crystalline in 2.5 g chitosan : 25.0 g TiO ₂ photocatalyst with different photocatalyst loading (1 to 6 dip-coating layers)	75
4.8	The FT-IR spectra of chitosan, TiO ₂ , and dried TiO ₂ -Chitosan catalyst (100 °C)	79
4.9	TG/SDTA curves of precursor TiO ₂ Degussa P 25 powder	85
4.10	TG/SDTA curves of raw chitosan	86
4.11	TG/SDTA curves of the prepared TiO ₂ -Chitosan catalyst (2.5 g of chitosan : 2.5 g of TiO ₂ Degussa P 25)	88
4.12	A plot of mean mass of TiO ₂ -Chitosan catalyst for 5 samples versus number of dip-coating repetition	91
4.13	A plot of Absorbance/A vs Wavelength/nm for λ_{\max} of MO at natural pH, pH 2-4 and pH 10-12	92
4.14	Standard calibration curves for MO (a) $\lambda_{\max} = 464.0$ nm (b) $\lambda_{\max} = 500.5$ nm	93
4.15	A plot of Absorbance/A vs Wavelength/nm for λ_{\max} of MB at natural pH, pH 2-4 and pH 10-12	95
4.16	Standard calibration curves for MB established based on $\lambda_{\max} = 664.0$ nm	96
4.17	Model pollutants stability against light photolysis, initial dye concentration ≈ 10 ppm at natural pH and temperature	97
4.18	Adsorption of MO using photocatalyst prepared by using different ratio of TiO ₂ : Chitosan (500 ml MO solution at 20 ppm)	101

4.19	Photodegradation of MO using photocatalyst prepared by using different ratio of TiO ₂ : Chitosan (500 mL MO solution at 20 ppm)	101
4.20	Effect of dip-coating repetition on the adsorption removal of 500 mL, 20 ppm MO	104
4.21	Effect of dip-coating repetition on the photodegradation removal of 500 mL, 20 ppm MO	105
4.22	Photodegradation-adsorption removal distribution of MO according to different dip-coating repetition	106
4.23	(a) Adsorption and (b) photodegradation removal kinetics of MO using photocatalyst with different dip-coating repetition (500 mL, 20 ppm)	113
4.24	Pseudo second kinetic order removal of MO using photocatalyst with different dip-coating repetition (a) Adsorption and (b) photodegradation, inset (1 layer)	118
4.25	Graphs 1 - C/Co vs Time, t/min for the (a) adsorption and (b) total / photodegradation removal of MO at different initial concentration	124
4.26	Graph ln C/Co vs Time, t/min for the effect of different initial concentration (a) adsorption and (b) total / photodegradation removal of MO	126
4.27	Graph 1 - C/Co vs Time, t/min for MO removal for the effect of light Intensity (500 mL, 20 ppm)	133
4.28	Graph ln C/Co vs Time, t/min for MO removal for the effect of light intensity fitting pseudo-first kinetic order model (500 mL, 20 ppm)	134
4.29	Graph 1 - C/Co vs Time, t/min for MO removal for experiments run under different light source irradiation (500 mL, 20 ppm)	137
4.30	Graph ln C/Co vs Time, t/min for MO removal for experiments run under different light source irradiation fitting pseudo first kinetic order (500 mL, 20 ppm)	138
4.31	Temperature dependence of MO removal (a) adsorption and (b) total / photodegradation removal process (500 mL, 20 ppm)	144
4.32	Graph ln C/Co vs Time, t/min indicating the temperature dependence of MO removal due to (a) adsorption and (b) total / photodegradation removal process fitting pseudo-first kinetic order model (500 mL, 20 ppm)	146
4.33	Graph ln C/Co vs Time, t/min indicating the pH dependence of MO	151

	removal due to (a) adsorption and (b) total / photodegradation removal process fitting pseudo-first kinetic order model (500 mL, 20 ppm)	
4.34	pH dependence of MO removal due to adsorption process (500 mL, 20 ppm)	152
4.35	pH dependence for the adsorption removal of MO closely fitting pseudo-second kinetic order model (500 mL, 20 ppm)	153
4.36	pH dependence for the total / photodegradation removal of MO (500 mL, 20 ppm)	158
4.37	pH dependence for the total / photodegradation removal of MO closely fitting pseudo-second kinetic order model (500 mL, 20 ppm)	159
4.38	pH dependence of MB removal due to adsorption process (500 mL, 20 ppm)	163
4.39	Graph $\ln C/C_0$ Vs Time, t/min showing the pH dependence of MB removal due to adsorption process fitting pseudo-first kinetic order model (500 mL, 20 ppm)	164
4.40	pH dependence for the total / photodegradation removal of MB (500 mL, 20 ppm)	167
4.41	Graph $\ln C/C_0$ Vs Time, t/min for the total / photodegradation removal of MB showing pH dependence mechanism closely follow pseudo-first kinetic order model (500 mL, 20 ppm)	168
4.42	Adsorption removal of MO in mixed dyes in different solution pH medium (500 mL, 20 ppm)	173
4.43	Adsorption removal of MB in mixed dyes in different solution pH medium (500 mL, 20 ppm)	174
4.44	Total / photodegradation removal of MO in mixed dyes in different solution pH medium (500 mL, 20 ppm)	176
4.45	Total / photodegradation removal of MB in mixed dyes in different solution pH medium (500 mL, 20 ppm)	177
4.46	Graphs 1 - C/C_0 vs Time, t/min showing comparison for the combined photodegradation-adsorption removal of MO and MB: pH 4.0 – 6.0 Dark (MO adsorption process), pH 4.0 – 6.0 UV (MO photodegradation process), pH 10.0 – 12.0 Dark (MB adsorption process), pH 10.0 – 12.0 UV (MB photodegradation process), 500 mL, 20 ppm	182

4.47	Graphs $\ln C/C_0$ versus Time, t/min following pseudo first kinetic order model for the combined photodegradation-adsorption removal of MO and MB: pH 4.0 – 6.0 Dark (MO adsorption process), pH 4.0 – 6.0 UV (MO photodegradation process), pH 10.0 – 12.0 Dark (MB adsorption process), pH 10.0 – 12.0 UV (MB photodegradation process), 500 mL, 20 ppm	183
4.48	Disappearance of total organic carbon and colour for MO versus Time, t/min for both of the photodegradation and adsorption processes	189
4.49	Temporal changes of the intermediates produced during the photodegradation-adsorption removal of MO under optimum condition	190
4.50	Disappearance of total organic carbon and colour for MB versus Time, t/min for both of the photodegradation and adsorption processes	193
4.51	Temporal changes of the intermediates produced during the photodegradation-adsorption removal of MB under optimum condition	194
4.52	(a) DI/MS chromatogram monitored in full scan corresponding to MO and its intermediates detection at time, $t = 0$ minute, three intermediate compounds were identified (peak 1, 2 and 3)	199
4.52	(b) DI/MS spectrum monitored in full scan corresponding to MO and its intermediates detection at time, $t = 0$ minute as referred to peak number 1	200
4.52	(c) DI/MS spectrum monitored in full scan corresponding to MO and its intermediates detection at time, $t = 0$ minute as referred to peak number 2	201
4.52	(d) DI/MS spectrum monitored in full scan corresponding to MO and its intermediates detection at time, $t = 0$ minute as referred to peak number 3	202
4.53	(a) DI/MS chromatogram monitored in full scan corresponding to MO and its intermediates detection at time, $t = 60$ minutes, four intermediate compounds were identified (peak 1, 2, 3 and 4)	203
4.53	(b) DI/MS spectrum monitored in full scan corresponding to MO and its intermediates detection at time, $t = 60$ minutes as referred to peak number 1	204

4.53	(c) DI/MS spectrum monitored in full scan corresponding to MO and its intermediates detection at time, t = 60 minutes as referred to peak number 2	205
4.53	(d) DI/MS spectrum monitored in full scan corresponding to MO and its intermediates detection at time, t = 60 minutes as referred to peak number 3	206
4.53	(e) DI/MS spectrum monitored in full scan corresponding to MO and its intermediates detection at time, t = 60 minutes as referred to peak number 4	207
4.54	(a) DI/MS chromatogram monitored in full scan corresponding to MO and its intermediates detection at time, t = 120 minutes, only one intermediate compounds was identified (peak 1)	208
4.54	(b) DI/MS spectrum monitored in full scan corresponding to MO and its intermediates detection at time, t = 120 minutes as referred to peak number 1	209
4.55	(a) DI/MS chromatogram monitored in full scan corresponding to MO and its intermediates detection at time, t = 240 minutes, four intermediate compounds were identified (peak 1, 2, 3 and 4)	210
4.55	(b) DI/MS spectrum monitored in full scan corresponding to MO and its intermediates detection at time, t = 240 minutes as referred to peak number 1	211
4.55	(c) DI/MS spectrum monitored in full scan corresponding to MO and its intermediates detection at time, t = 240 minutes as referred to peak number 2	212
4.55	(d) DI/MS spectrum monitored in full scan corresponding to MO and its intermediates detection at time, t = 240 minutes as referred to peak number 3	213
4.55	(e) DI/MS spectrum monitored in full scan corresponding to MO and its intermediates detection at time, t = 240 minutes as referred to peak number 4	214
4.56	(a) DI/MS chromatogram monitored in full scan corresponding to MO and its intermediates detection at time, t = 360 minutes, two intermediate compounds were identified (peak 1 and 2)	215

4.56	(b) DI/MS spectrum monitored in full scan corresponding to MO and its intermediates detection at time, $t = 360$ minutes as referred to peak number 1	216
4.56	(c) DI/MS spectrum monitored in full scan corresponding to MO and its intermediates detection at time, $t = 360$ minutes as referred to peak number 2	217
4.57	(a) DI/MS chromatogram monitored in full scan corresponding to MB and its intermediates detection at time, $t = 0$ minute, two intermediate compounds were identified (peak 1 and 2)	222
4.57	(b) DI/MS spectrum monitored in full scan corresponding to MO and its intermediates detection at time, $t = 0$ minute as referred to peak number 1	223
4.57	(c) DI/MS spectrum monitored in full scan corresponding to MB and its intermediates detection at time, $t = 0$ minute as referred to peak number 2	224
4.58	(a) DI/MS chromatogram monitored in full scan corresponding to MB and its intermediates detection at time, $t = 60$ minutes, two intermediate compounds were identified (peak 1 and 2)	225
4.58	(b) DI/MS spectrum monitored in full scan corresponding to MB and its intermediates detection at time, $t = 60$ minutes as referred to peak number 1	226
4.58	(c) DI/MS spectrum monitored in full scan corresponding to MB and its intermediates detection at time, $t = 60$ minutes as referred to peak number 2	227
4.59	(a) DI/MS chromatogram monitored in full scan corresponding to MB and its intermediates detection at time, $t = 120$ minutes, two intermediate compounds were identified (peak 1 and 2)	228
4.59	(b) DI/MS spectrum monitored in full scan corresponding to MB and its intermediates detection at time, $t = 120$ minutes as referred to peak number 1	229
4.59	(c) DI/MS spectrum monitored in full scan corresponding to MB and its intermediates detection at time, $t = 120$ minutes as referred to peak number 2	230



4.60	(a) DI/MS chromatogram monitored in full scan corresponding to MB and its intermediates detection at time, $t = 240$ minutes, two intermediate compounds were identified (peak 1 and 2)	231
4.60	(b) DI/MS spectrum monitored in full scan corresponding to MB and its intermediates detection at time, $t = 240$ minutes as referred to peak number 1	232
4.60	(c) DI/MS spectrum monitored in full scan corresponding to MB and its intermediates detection at time, $t = 240$ minutes as referred to peak number 2	233
4.61	(a) DI/MS chromatogram monitored in full scan corresponding to MB and its intermediates detection at time, $t = 360$ minutes, two intermediate compounds were identified (peak 1 and 2)	234
4.61	(b) DI/MS spectrum monitored in full scan corresponding to MB and its intermediates detection at time, $t = 360$ minutes as referred to peak number 1	235
4.61	(c) DI/MS spectrum monitored in full scan corresponding to MB and its intermediates detection at time, $t = 360$ minutes as referred to peak number 2	236

LIST OF ABBREVIATIONS/NOTATIONS/GLOSSARY OF TERMS

ASAP	Analysis of Surface Area and Porosity
b	constant related to the energy of sorption
C_0	initial concentration of dye in solution
cb	conduction band
C_e	equilibrium concentration of dye
C_t	dye concentration in solution at time t
DI/MS	Direct Insertion / Mass Spectroscopy
FT-IR	Fourier Transform Infrared Spectroscopy
GC/MS	Gas Chromatography / Mass Spectroscopy
k	initial sorption rate
k_{app}	apparent rate constant
L	litre
MB	Methylene blue
MD	Mixed dyes
min	minute(s)
mL	mililitre
μL	microlitre
MO	Methyl orange
M_w	molecular weight
q_e	amount of dye adsorbed on the surface of the sorbent at equilibrium
q_t	amount of dye adsorbed on the surface of time t



R^2	correlation coefficient
SEM-EDX	Scanning Electron Microscopy coupled with Energy Dispersive X-ray analysis
t	time
$t_{1/2}$	half life
TGA	Thermogravimetric Analysis
UV/vis	Ultra violet/visible spectrometer analysis
vb	valence band
vs	versus
XRD	X-ray diffractometry



Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Doctor of Philosophy

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Chairman : Professor Zulkarnain Zainal, PhD

Faculty : Science

The combination effect of photodegradation-adsorption using the immobilized TiO₂ and chitosan supported on glass (TiO₂-Chitosan/Glass) under the illumination of light with suitable energy ($h\nu > E_{bg}$) as a new method for the treatment or pre-treatment of dye-containing wastewater has been studied. The prepared photocatalyst was characterized by scanning electron microscopy, X-ray microanalysis, X-ray diffraction analysis, Fourier transform infrared spectroscopy, surface area and porosimetry analysis and thermogravimetric analysis.

Methyl orange (an anionic dye of the monoazo series) removal was studied based on the effect of TiO₂ : Chitosan ratio, photocatalyst loading, initial concentration, light intensity, different light source, temperature and pH. Comparison was also made to dyes with different characteristics, namely methylene blue (a cationic dye) and mixed dyes (a mixture of methyl orange and methylene blue). Methyl orange removal was optimum when the experiment was run using 5 pieces of 4 dip-coated TiO₂-Chitosan/Glass (45 mm X 80 mm X 2 mm) and 500



ml of 20 ppm methyl orange solution at 40 °C under the illumination of a 230 V near UV lamp for 6 hours.

About 87.0 % of 20 ppm methyl orange can be removed successfully with approximately 9.2 % removal efficiency attributable to photodegradation process and another 77.8 % attributable to adsorption process. Comparatively, approximately 93.8 % or 18.51 ppm of methylene blue can be removed by applying the same condition with approximately 43.7 % removal efficiency attributable to photodegradation process and another 50.1 % attributable to adsorption process.

The solution pH was found to have a significant and yet complex effect. Solutions with pH 4.0 – 6.0 and 10.0 – 12.0 were found to be the optimum range for methyl orange and methylene blue respectively. In view of the electrostatic attraction between the catalyst and substrates, the ionic characteristic of the dyes is suggested to play an important and selective role in both the photodegradation and adsorption processes. The adsorption of model pollutant solutes on the prepared TiO₂-Chitosan photocatalyst surface leads to the effective photodegradation process.

Removal rate of methyl orange and methylene blue were studied based on the integrated form of Langmuir-Hinshelwood kinetic equations. The photodegradation-adsorption process obeys first order kinetics for the first 60 minutes. After that, it was most likely to be affected by the solution pH and the nature of the photocatalyst. This is obvious based on the effect of pH for

MO and MB removal, in which the obtained data cannot fit nicely into the kinetic model or its linearized form.

Although Total Organic Carbon (TOC) and Gas Chromatography-Mass Spectrometry (GS/MS) coupled with Direct Insertion-Mass Spectrometry (DI/MS) analyses had confirmed the successful break up of methyl orange and methylene blue 'parent molecule', successful destruction of methylene blue aromatic rings is quite difficult to achieve. Nevertheless, the combined photodegradation-adsorption system still appears to be an efficient accelerated removal process of organic pollutants from waste water.



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**FOTODEGRADASI-JERAPAN PEWARNA ORGANIK MENGGUNAKAN
KITOSAN TERDOKONG PEMANGKIN CAHAYA TITANIUM DIOKSIDA**

Oleh

LEE KONG HUI

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Pengerusi : Profesor Zulkarnain Zainal, PhD

Fakulti : Sains

Gabungan kesan fotodegradasi-jerapan menggunakan TiO_2 dan kitosan terdokong di atas kepingan kaca (TiO_2 -Kitosan/Kaca) di bawah penyinaran cahaya dengan tenaga yang sesuai ($h\nu > E_{bg}$) sebagai satu kaedah baru perawatan dan pra-perawatan air tercemar yang mengandungi bahan pewarna telah dikaji. Pencirian bahan pemangkin yang disediakan dilakukan melalui mikroskopi pengimbasan elektron, mikroanalisis sinar-X, analisis pembelauan sinar-X, spektroskopi inframerah transformasi Fourier, analisis luas permukaan dan keliangan dan analisis termogravimetri.

Penyingkiran metil jingga (sejenis pewarna anion daripada siri monoazo) telah diselidiki berdasarkan kepada kesan nisbah TiO_2 :Kitosan, jumlah bahan pemangkin yang didokongkan, kepekatan larutan, keamatan cahaya, sumber cahaya yang berbeza, suhu larutan, dan pH. Perbandingan juga dilakukan dengan pewarna yang mempunyai sifat yang berbeza, iaitu metilina biru (pewarna kation) dan pewarna campuran (campuran metil jingga dan metilina biru). Penyingkiran optimum metil jingga dicapai apabila eksperimen dijalankan dengan menggunakan 5 keping pemangkin TiO_2 -Kitosan/Kaca (45 mm X 80 mm X 2 mm) yang

dicelupkan sebanyak 4 kali dengan kepekatan larutan awal metil jingga 20 ppm pada suhu 40 °C di bawah sinaran cahaya hampir UV 230 V selama 6 jam.

Lebih kurang 87.0 % daripada 20 ppm metil jingga berjaya disingkirkan dengan sejumlah 9.2 % kesan penyingkiran dihasilkan oleh proses fotodegradasi, manakala 77.8 % adalah sumbangan daripada proses jerapan. Secara perbandingannya, lebih kurang 93.8 % atau 18.51 ppm metilina biru juga boleh disingkirkan dengan menggunakan kaedah yang sama dengan sejumlah 43.7 % kesan penyingkiran dihasilkan oleh proses fotodegradasi, manakala 50.1 % yang lain disumbangkan oleh proses jerapan..

Keadaan pH larutan telah dikenalpasti mempunyai kesan yang ketara dan kompleks. Larutan dengan pH 4.0 – 6.0 dan 10.0 – 12.0 telah dikenalpasti sebagai julat pH optimum untuk metil jingga dan metilina biru. Berlandaskan kepada teori tarikan elektrostatik yang wujud di antara pemangkin dan substrat, sifat ionik bahan pewarna dicadangkan berkemungkinan memainkan peranan pilihan yang penting dalam kedua-dua proses fotodegradasi dan jerapan. Jerapan bahan substrat di atas permukaan bahan fotomangkin TiO₂-Kitosan akan membawa kepada proses fotodegradasi yang berkesan.

Kadar penyingkiran metil jingga dan metilina biru telah dikaji berdasarkan kepada persamaan kinetik Langmuir-Hinshelwood terubahsuai. Penyingkiran melalui fotodegradasi-jerapan didapati mematuhi kinetik tertib pertama untuk 60 minit yang pertama. Selepas tempoh itu, besar kemungkinan ia akan dipengaruhi oleh pH larutan dan tabii fotomangkin yang digunakan. Keadaan ini jelas ditunjukkan berdasarkan kepada kajian kesan pH terhadap

penyingkiran metil jingga dan metilina biru, di mana data yang diperoleh tidak dapat dipadankan kepada model kinetik atau bentuknya yang terubahsuai.

Sungguhpun analisis Jumlah Karbon Organik (TOC) dan Kromatografi Gas-Spektrometri Jisim (GC/MS) yang dilengkapi dengan Selitan Terus-Spektrometri Jisim (DI/MS) telah mengesahkan pemecahan 'molekul sumber' metil jingga dan metilina biru, akan tetapi pemecahan gelang aromatik metilina biru adalah sukar dicapai. Walau bagaimanapun, gabungan sistem fotodegradasi-jerapan ini masih merupakan proses penyingkiran pantas bahan pencemar organik dalam air yang berkesan.