UNIVERSITI PUTRA MALAYSIA

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

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DOCTOR OF PHILOSOPHY
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By

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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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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
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By

LEE KONG HUI

June 2007

Chairman : Professor Zulkarnain Zainal, PhD

Faculty : Science

The combination effect of photodegradation-adsorption using the immobilized TiO_2 and chitosan supported on glass (TiO_2-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 TiO_2 : 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 TiO_2-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 TiO_2-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.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

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

Oleh

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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 ($h\upsilon > E_{bg}$) 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 subtrat di atas permukaan bahan fotomangkin TiO_2-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 dilengkapkan 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.