



UNIVERSITI PUTRA MALAYSIA

**PHOTODEGRADATION AND ADSORPTION OF FAST GREEN FCF
IN TiO_2 -CHITIN SUSPENSION**

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FS 2005 26

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TiO₂-CHITIN SUSPENSION**

By

FATIMAH JULIA ROMELI

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

April 2005



*To my husband, my daughter,
my parents, and my family,
With all my heart and love
For all that you are, what you do
and what you mean to me.
Thank you can't ever quantify the sacrifices.*



Abstract of the thesis presented to the Senate of Universiti Putra Malaysia in
fulfilment of the requirements for the degree of Master of Science

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Chairman : Professor Zulkarnain Zainal, PhD

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The potential of chitin as co-adsorbent in the photocatalytic degradation of Fast Green in titanium dioxide suspension was investigated. The physico-chemical characteristics of chitin were studied using Analysis of Surface Area and Porosity (ASAP), Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM).

The sorption study was first done and compared with titanium dioxide heterogeneous photocatalysis. The result of kinetics studies indicates that the sorption process was pH dependent and exothermic. The adsorption equilibrium was achieved after 60 minutes and the adsorption capacity increased as the dye concentration was increased. The kinetic data was tested for first and pseudo-second kinetic order models and was found to fit well to the latter, while the adsorption isotherm was found to agree well with the Langmuir equation assuming monolayer type adsorption.

The photocatalytic degradation and adsorption of Fast Green from aqueous solution has been investigated in suspensions containing commercial titanium dioxide (Degussa P-25), chitin and mixture of titanium dioxide-chitin. The removals of Fast Green using a mixture of titanium dioxide-chitin were found to follow first order kinetic. The presence of chitin in titanium dioxide suspension enhanced the removal by two times higher. Fast Green removal using mixture of titanium dioxide-chitin under UV irradiation was found to be more efficient rather than illumination using titanium dioxide or chitin alone.

The removal of Fast Green using chitin and a mixture of titanium dioxide-chitin were rapid for the first 30 minute and reached equilibrium after 1 hour. A synergy effect was observed with an increase in the apparent rate constant by 1.86 times. This was ascribed to an extended adsorption of Fast Green on chitin followed by a transfer to titanium dioxide where it is photocatalytically degraded.

pH has significant effect on the adsorption and photodegradation properties of chitin and titanium dioxide surface. However, the effect of temperature on adsorption and photodegradation process using titanium dioxide-chitin mixture was minimal. This combined photocatalytic-adsorption system appears promising as an efficient accelerated removal process of organic pollutants from water.

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

**FOTODEGRADASI DAN JERAPAN *FAST GREEN FCF* DI DALAM
AMPAIAN TiO_2 -KITIN**

Oleh

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April 2005

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Keupayaan kitin sebagai pembantu jerapan dalam degradasi fotomangkin heterogen *Fast Green* dalam ampaian titanium dioksida telah dikaji. Sifat-sifat kimia-fizik kitin telah dikaji menggunakan Analisis Luas Permukaan dan Keliangan (ASAP), Spektroskopi Infra Merah (FTIR) dan Mikroskop Pengimbas Elektron (SEM).

Kajian jerapan yang dilakukan telah dibandingkan dengan fotomangkin heterogen menggunakan titanium dioksida. Kajian kinetik menunjukkan proses erapan dipengaruhi oleh pH dan bersifat eksotermik. Erapan maksimum diperolehi selepas 60 minit dan kapasiti erapan meningkat dengan peningkatan kepekatan *Fast Green*. Data dari kajian kinetik juga telah disuaipadan untuk kinetik tindak balas tertib pertama dan *pseudo*-kedua. Didapati, ia sesuai dengan kinetik tindak balas *pseudo*-kedua, sementara jerapan isoterma didapati mematuhi persamaan Langmuir, dengan anggapan jerapan berlaku pada satu lapisan sahaja.

Degradasi fotomangkin dan jerapan *Fast Green* dari larutan akueus telah dikaji dalam ampaian yang mengandungi titanium dioksida komersil (Degussa P-25), kitin dan campuran titanium dioksida-kitin. Penyingkiran *Fast Green* menggunakan campuran titanium dioksida-kitin didapati mematuhi tertib tindak balas pertama. Kehadiran kitin dalam ampaian titanium dioksida meningkatkan penyingkiran sebanyak dua kali ganda. Penyingkiran *Fast Green* menggunakan campuran titanium dioksida-kitin dengan sinaran lampu UV didapati sangat berkesan berbanding dengan penyingkiran menggunakan titanium dioksida atau kitin sahaja.

Penyingkiran *Fast Green* menggunakan kitin dan campuran titanium dioksida-kitin berlaku sangat cepat dalam tempoh masa 30 minit yang pertama dan mencapai keseimbangan selepas 1 jam. Kesan tenaga dapat dilihat melalui peningkatan kadar tetap sehingga 1.86 kali. Ini dapat dijelaskan melalui jerapan tambahan oleh kitin diikuti oleh pemindahan kepada titanium dioksida di mana ia akan didegradasi oleh fotomangkin.

pH mempunyai kesan yang penting ke atas sifat-sifat jerapan dan fotodegradasi ke atas permukaan titanium dioksida dan kitin. Walaubagaimanapun, kesan suhu adalah sangat minima ke atas proses jerapan dan fotodegradasi menggunakan campuran titanium dioksida-kitin. Gabungan sistem jerapan-fotodegradasi ini, menjanjikan keberkesanan dalam proses penyingkiran pantas bahan pencemar organik dalam air.

ACKNOWLEDGMENTS

I would like to express my appreciation to my supervisor, Prof. Dr. Zulkarnain Zainal and co-supervisors, Prof. Dr. Mohd Zobir bin Hussein, Assoc. Prof. Dr. Mohamad Zaki Ab Rahman and Assoc. Prof. Dr. Asmah Hj Yahaya for their invaluable assistance, advice, guidance and patience throughout the duration of the project.

I would like to take this opportunity to extend my deepest appreciation to all the staff in the Chemistry Department for their assistance and cooperation in one way or another that has contributed to the success of this study.

My sincere gratitude is also extended to Saravanan, Lee Kong Hui, Salina, Mazlina, Mazidah, Adilla and all laboratory members and friends for their helps throughout this project and providing appropriate assistance.

Finally, financial support from IRPA funding (09-02-04-0255-EA001) is gratefully acknowledged.

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LIST OF SYMBOLS AND ABBREVIATIONS

AC	activated carbon
AR14	Acid Red 14
ASAP	Analysis of Surface Area and Porosity
b	constant related to the energy of sorption
BET	Brunauer-Emmet-Teller
cb	conduction band
C_e	equilibrium concentration of dye
C_0	initial concentration of dye in solution
C_t	dye concentration in solution at time t
D_c	diffusion coefficient of the charged carrier
e^-	electron
E_a	activation energy
E_g	energy gap
FG	Fast Green FCF
FTIR	Fourier Transform Infrared Spectroscopy
h^+	positive holes
l	penetration distance of the light
k	initial sorption rate
k_{app}	apparent rate constant
N^*	maximum sorption of the system
N_e	amount of dye sorbed by sorbent at equilibrium
N_0	sorption capacity

q_e	amount of Fast Green sorbed on the surface of the sorbent at equilibrium
q_t	amount of Fast Green sorbed on the surface of time, t
R	radius of the particle
R^2	correlation coefficient
SEM	Scanning Electron Microscope
t	time
$t_{1/2}$	half life
UV	ultra violet
vb	valence band
α	reciprocal absorption length
λ	wavelength
λ_g	threshold wavelength
λ_{max}	maximum wavelength

CHAPTER I

INTRODUCTION

Water is the most abundant natural resource on earth. It is also the living environment for a large proportion of the earth's animals and plants. Essential to most human activities, it can mean life or death, bounty or poverty, war or peace. Water is commonly taken for granted as nature's gift. Not only because of wasteful usage, but industry and people pollute and poison available water supplies at a frightening rate. Water problems are centuries old. Water pollution occurs when substances are added to the water causing a detrimental alteration to its physical, chemical, biological or anesthetic characteristic. Pollutants are either foreign substances or natural substances discharged in excessive amounts.

Various treatment strategies are applied for the removal of toxic organic pollutants from water. The conventional method for water treatment which included chemical precipitation, chemical oxidation or reaction, ion exchange, electrochemical treatment, nanofiltration, ozonation, combustion, among others, are efficient but has inherent limitations in applicability, effectiveness and cost. Heterogeneous photocatalysis using TiO_2 as photocatalyst recently emerged as an efficient purifying method. Several attempts have been made to increase its photoefficiency either by noble metal deposition (Breuer and Wilke, 1999) or by ion doping (Herrmann et al., 1984), but such modification did not enhance the photocatalytic activity and were rather detrimental.

Conceptually, combination of more than one processes such as photodegradation and adsorption, would provide a viable solution to this problem. Sorption is one of the several techniques that have been successfully employed for effective dye removal. Therefore, another way to increase the photocatalytic efficiency of TiO_2 consists of adding a co-adsorbent such as silica, alumina, zeolite, clay or activated carbon (Tanguay et al., 1989, Ilisz, et al., 2004 and Takeda et al., 1998).

However, due to the high cost involved and considering the great amount of contaminated water, research has recently directed towards alternative co-adsorbents, namely low cost adsorbent, including the utilization of waste materials. Furthermore, fly ash, clay and sawdust are inexpensive but poor sorbents, while some other materials fail for other reasons, for instance, activated alumina is effective in removing heavy metals, but it readily soluble under extreme pH condition (Sağ and Aktay, 2002).

Therefore, the idea of using natural waste material from the seafood industry, such as shrimp shells rises in this context. Shrimp shells contain a natural biopolymer, chitin, which has been studied as adsorbent for textile dyestuff (Loureiro et al., 2000). Chitin is considered as low cost adsorbents because it can be extracted in large quantities from crab and shrimp shells, saving the cost involved in land filling the tons of crab and shrimp shells piling up along coastlines or from the broth of industrial fungal processes (Zhou et al., 1999).

During the past twenty years, great efforts have been made to apply chitin in chemical engineering and biomedical applications, including water treatment, metal

accumulation and recovery, as well as functional membranes, and the control of necessary metal elements in the human body.

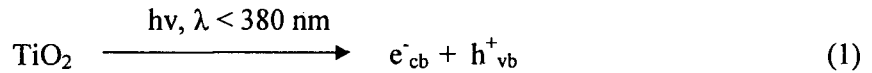
A series of works on the effects of adding co-adsorbents, mainly activated carbon (Faria and Gomez da Silva, 2003, Matos et al., 1998, Ilisz et al., 2002, Herrmann et al., 1999), in aqueous suspended mixtures with TiO_2 for photocatalytic degradation has attract the attention to study the effect of other adsorbent such as chitin. Different adsorbent induces different effects suggesting that the properties of the co-adsorbent may play a significant role upon the photoefficiency of the associated TiO_2 .

SEMICONDUCTOR PHOTOCATALYSIS

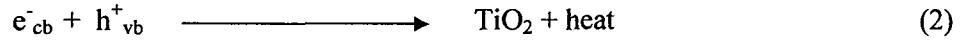
Photocatalysis can be defined as the acceleration of a photoreaction by the presence of a catalyst (Mills and Hunte, 1997). Photocatalysis over a semiconductor oxide such as TiO_2 is initiated by the absorption of a photon with energy equal to or greater than the band gap of the semiconductor producing electron-hole (e^-/h^+) pairs. The band gap energy for TiO_2 is 3.2 eV (Nogueira and Wilson, 1993).

Absorption of light with $\lambda < 380 \text{ nm}$ by TiO_2 excites electrons on the valence band (vb) to the conduction band (cb) with the generation of a positive hole in the valence band. The valence band hole is strongly oxidizing and the conduction band electron is strongly reducing. Most of the electron and hole recombine but those reaching the surface of the pigment particles can react to produce free-radical species.

The formation of electron-hole pairs can be represented via:



A fraction of electron-hole pair produced may also recombine to produce heat or light.



Other fraction of electron-hole pairs that do not recombined may migrate to the surface of the semiconductor, where they can undergo reduction and oxidation reactions.

Consequently, following irradiation, the TiO_2 particle can act as either an electron donor or acceptor for molecules in the surrounding media. However, the photoinduced charge separation in bare TiO_2 particles has a very short lifetime because of charge recombination. Therefore, it is important to prevent hole-electron recombination before a designated chemical reaction occurs on the TiO_2 surface. This charge recombination is demonstrated in Figure 1, where major processes occurring on a photogenerated semiconductor particle include:

- i) Electron-hole recombination at the surface (reaction a).
- ii) Electron-hole recombination in the bulk of the semiconductor (reaction b).
- iii) At the surface of the particle, photo generated electrons reduce an electron acceptor a (reaction c).
- iv) Photogenerated holes oxidize an electron donor D (reaction d).

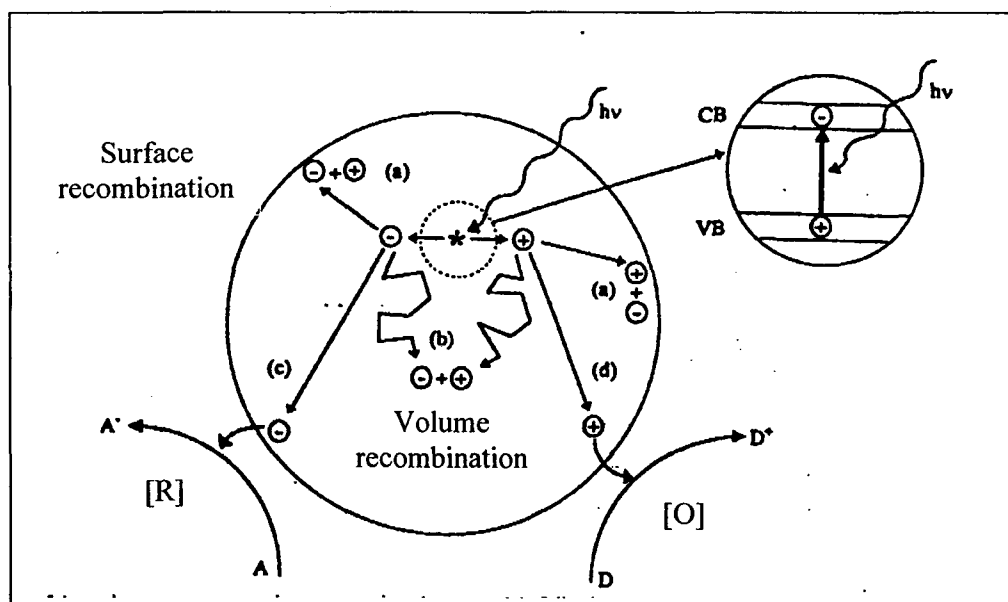
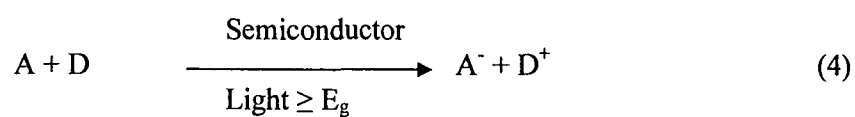


Figure 1: Charge recombination (Mills and Hunte, 1997)

However, Gerisher and Heller, (1990) assumed that hole can escape from the recombination. The average transit time to the surface for the electronic charge carriers generated by light absorption is

$$\tau_D \approx R^2/\pi^2 D_c \quad (3)$$

Where R is the radius of the particle and D_c is the diffusion coefficient of the charged carrier. The combination of the reaction (c) and (d) represents the general redox reduction:

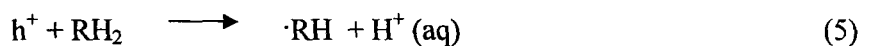


Photodegradation reaction on the surface of semiconductor may proceed via:

- 1) production of electron-hole pairs, photogenerated by exciting the semiconductor with light of energy greater than band gap energy.
- 2) separation of electrons and holes by traps available on the semiconductor surface, with a rate greater than the recombination rate.
- 3) redox processes induced by the separated electrons and holes with adsorbates present on the surface.
- 4) desorption of the product and reconstruction of the surface.

ROLE OF OXYGEN

Gerisher and Heller, (1990) analyzed the role of oxygen in photooxidation of organic molecules on semiconductor particles. Photoexcitation of semiconductors results in the formation of electron-hole pairs. Since hole transfer to adsorbed organic molecules or to water is very fast, two-electron transfer to O_2 may become the rate limiting factor. In n-type semiconductors, the more reactive species are the holes, which carry the major part of energy of the light quantum. The holes may either react by recombination with electrons (thus lowering the quantum efficiency), or they may react with organic molecules, RH_2 ,



as well as with surface-adsorbed OH^- anions, forming hydroxyl radicals,



Electrons usually react more slowly than hole. The known variability in the photocatalytic efficiency of TiO₂ prepared by various methods may be due to differences in the distribution of surface traps, on which electrons are immobilized.

Since holes at the particle interface usually react faster than electrons, the particles under illumination contain an excess of electrons. Removal of these excess electrons is necessary to complete the oxidation reaction, by preventing the recombination of electrons with holes. The most easily available and economic electron acceptor is molecular oxygen. Thus, in the presence of air or oxygen, the predominant reaction of electrons with O₂ is:



Oxygen diffusion was shown not to be the rate-limiting factor in the case of illumination of n-TiO₂ particles in water under sunlight. For TiO₂ particles larger than 1 μm, the rate of electron transfer to adsorbed O₂ may be the limiting factor, resulting in losses of quantum efficiency. The catalytic effect of noble metal catalyst on TiO₂ particles could possibly be due to their facilitating nature of electron transfer from the particles to molecular oxygen. The rate-controlling process in oxygen reduction on illuminated semiconductor particles has been proposed by Gerisher and Heller (1990) to be electrons trapped near the surface of the particles, which may transfer to surface-adsorbed oxygen molecules. Therefore, highly efficient photooxidation of organic molecules requires fast O₂ reduction, which may be achieved by incorporating catalytic sites on the TiO₂ surface.