UNIVERSITI PUTRA MALAYSIA

PHOTODEGRADATION OF DYES USING TITANIUM DIOXIDE SUPPORTED ON GLASS

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By

LEE KONG HUI

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

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DEDICATION

I would like to dedicate my work to both my beloved parents for their full support to carry out my Master Degree Study in Universiti Putra Malaysia.

Abstract of 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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Faculty : Science and Environmental Studies

Photodegradation of dyes, in aqueous solution was carried out using titanium dioxide coated on glass plates, illuminated by blue fluorescent lamps. TiO_2 coated glass was prepared by sol-gel technique. Air was pumped into the mixture to ensure continuous supply of oxygen in the mixture.

Methylene blue removal was studied based on the effect of amount of coated TiO_2 sol-gel, initial concentration, light intensity, light source, and pH of solution medium. Comparison was also made to the powder form of TiO_2 which was prepared by the same method. The highest percentage of methylene blue removal was obtained when the photodegradation experiment was run using 5 pieces of TiO_2/Glass (4 times of sol-gel dip-coating) and 10 ppm of methylene blue solution at 28 °C after illumination under 4 white fluorescent lamps of 20 W for 4 hours. About 84 % of methylene blue was removed. Methylene blue removal was found to be efficient and comparable to the illumination using near UV light, sunlight, 4 white fluorescent lamps, 4 dark fluorescent lamps and 4 blue fluorescent lamps.

The best set of parameters for photodegradation process, such as the photocatalyst loading, initial concentration, light intensity, light source, and solution pH condition was determined. These parameters were used for the photodegradation process of methyl orange, chicago sky blue 6B, indigo carmine, mixed dyes (consist of methylene blue, methyl orange, chicago sky blue 6B, and indigo carmine), and industrial waste solution. Intermediates formed in the reaction pathway during photomineralization of methylene blue, methyl orange, indigo carmine, chicago sky blue 6B, mixed dyes, and industrial waste solution were analysed using High Performance Liquid Chromatography (HPLC) and Total Organic Carbon (TOC) analysers.

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

FOTODEGRADASI PEWARNA-PEWARNA MENGGUNAKAN KACA TERDOKONG TITANIUM DIOKSIDA

Oleh

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Julai 2002

Pengerusi : **Profesor Madya Zulkarnain Zainal, Ph.D.**

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Fotodegradasi pewarna dalam larutan akueus telah dikaji dengan menggunakan kaca terdokong TiO_2 (TiO_2/kaca) di bawah penyinaran lampu berpendaflor biru. Kaca terdokong TiO_2 disediakan dengan teknik sol-gel. Udara dipamkan masuk secara berterusan ke dalam larutan campuran untuk memastikan pembekalan gas oksigen yang secukupnya secara berterusan.

Kadar penyingkiran metilena biru telah dikaji berdasarkan kesan jumlah sol-gel TiO_2 yang telah didokongkan (kuantiti kaca yang telah digunakan), kepekatan awal, keamatan cahaya, sumber cahaya, dan keasidan medium larutan. Perbandingan juga dibuat terhadap penggunaan TiO_2 dalam bentuk serbuk. 5 keping TiO_2/kaca didapati memberikan kadar penyingkiran metilena biru paling tinggi. Lebih kurang 84 % daripada larutan berkepekatan 10 ppm telah disingkirkan pada suhu 28 °C apabila disinar oleh 4 lampu berpendaflor putih berkuasa 20 W selama 4 jam. Dapat diketahui juga bahawa kadar penyingkiran metilena biru adalah berkesan dan setanding untuk penyinaran dengan menggunakan cahaya dekat UV, cahaya matahari, 4 lampu berpendaflor putih, 4 lampu berpendaflor gelap, dan 4 lampu berpendaflor biru.

Satu set parameter terbaik untuk proses fotodegradasi telah ditentukan. Ia telah digunakan untuk proses fotodegradasi metil oren, indigo karmina, chicago ski biru 6B, pewarna campuran (terdiri daripada metilena biru, metil oren, indigo karmina, dan chicago ski biru 6B), dan larutan sisa organik kilang. Bahan perantaraan yang terbentuk dalam proses tindak balas semasa fotomineralisasi metilena biru, metil oren, indigo karmina, chicago ski biru 6B, pewarna campuran, dan air buangan kilang telah dianalisis dengan menggunakan penganalisis Kromatografi Cecair Prestasi Tinggi (HPLC) dan Jumlah Karbon Organik (TOC).

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This thesis submitted to the Senate of Universiti Putra Malaysia has been accepted as partial fulfilment of the requirements for the degree of Master of Science. The members of the Supervisory Committee are as follows.

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LIST OF ABBREVIATIONS

MB	methylene blue
MO	methyl orange
IC	indigo carmine
CSB	chicago sky blue 6B
VB	valence band
CB	conduction band
SEM	scanning electron microscope
EDX	energy dispersive X-ray spectrometer
TiO_2/Glass	titanium dioxide coated on glass
XRD	X-ray diffractometer or X-ray diffraction photometer
FT-IR	Fourier Transform-Infra Red
MO	molecular orbital
AO	atomic orbital
Mw	molecular weight

CHAPTER 1

INTRODUCTION

Potable water is a must for our life. The water that we use must be safe and free from apparent turbidity, colour, odour or any objectionable taste. However, there is a rising concern nowadays for the continuous supply of potable water due to the pollution of the water source arising as inevitable byproducts from industrial processes, agricultural treatment of crops and accidental spills or leaks from containers. One of the main pollution source of wastewater comes from the dyeing and finishing processes.

The textile industry consumes considerable amounts of water during the dyeing and finishing operations. Dyes are extensively used, hence wastewaters discharged in rivers or public sewage treatment plants are highly contaminated. Dyes are highly coloured organic substances. Thus, the presence of very small amounts of dyes in water will affect the aesthetic nature of water. Besides, the polluted wastewater is sometimes found to be carcinogenic and mutagenic. However, colour substances in dyeing effluents normally cause certain difficulties in traditional biological treatment processes due to their nonbiodegradable nature. Thus, it is necessary to remove colour from dyeing effluents with the help of some physical or chemical treatment processes (Li and Zhang, 1996 and Baker *et al.*, 2000).

Over the past decade, various methods have been developed to remove contaminant in wastewater. Biodegradable organic substances can be removed using biological treatment. Chemical means of removing contaminant in wastewater involve the addition of chemicals or by other specific chemical reactions, while the physical ways of wastewater contaminant removal consist of screening, mixing, filtration, gas transfer, floatation, sedimentation, and flocculation.

Presently, photocatalytic mineralisation of pollutants, especially organic pollutants had gained much attention. Photocatalysis is the acceleration of a photoreaction by the presence of a catalyst (Mills and Hunte, 1997). It involved the heterogeneous photocatalytic degradation of pollutants using semiconductors. In this regard, much attention has been focused on titanium dioxide (TiO_2) particles since this semiconductor is stable with respect to anodic dissolution (Zang *et al.*, 1995). It is non-toxic, insoluble, comparatively cheap, is available in some forms having high photoactivity and it can be activated by sunlight.

Investigation of the photochemical processes taking place in titanium dioxide/organic dyes systems is of considerable practical interest not only for the development of the processes involved in the purification of industrial effluents but also because the adsorbed dyes can sensitize photocatalysts and semiconducting materials based on titanium dioxide to light in the near UV and visible regions (Khalyavka *et al.*, 2001).

It has been found that titanium dioxide illuminated with light energy greater than bandgap energy ($\lambda < 380$ nm) can act as photocatalyst to mineralize toxic and bioresistant organic compounds from aqueous solution to non-toxic and safer compounds, namely mineral acids, carbon dioxide and water before it is releases into the environment. Specifically, it should also be effective to photomineralize commercial dyes such as methylene blue, methyl orange, and indigo carmine to mineral acids, carbon dioxide and water.

Titanium dioxide was supported on glass to avoid filtration and resuspension problem associated with the used of catalyst suspension before the water was discharged into the environment. Furthermore, the removal rate of the pollutants can also be enhanced by anchoring titanium dioxide on supports including zeolite (Xu and Langford, 1995), sand (Matthews, 1991), silica and activated carbon (Torimoto *et al.*, 1996) and glass matrix (Al-Ekabi and Serpone, 1988).

1.1 Theory of Semiconductor

Generally, a semiconductor can be defined as a substance having electrical conductivity between metals and insulators. Metal is a good electric and heat conductor, while semiconductor has a lower conductivity than that typical of metals. However, the magnitude of the conductivity is not the criterion of the distinction.

The electronic conduction in a solid can be explained with the help of Molecular Orbital (MO) Theory. We can define two kinds of electrons in a semiconductor; bonded and unbonded or free electrons. The electrons in a semiconductor will be distributed among the same number of MO formed as a linear combination of atomic orbital (LCAO).

In a semiconductor such as TiO_2, free electron energies are quantised in a large number of closely spaced energy levels and formed the conduction band (CB). The covalence bonds' electrons of a semiconductor also have a range of permitted energies.

These levels are also closely spaced and form an energy band called the valence band (VB). There is a gap between these two bands where there are no orbitals. The band gap acts as a barrier to electronic mobility. The energy levels of the CB is located above the energy levels of the VB.

Electrons are freed when they acquire enough energy and leave behind them gaps in the bonds, called holes (h^+). Band gap energy (E_g) is the absolute minimum energy required to promote electrons from the highest level of VB to the lowest level of CB. This can be represented in the energy levels diagram by a gap between VB and CB (Figure 1.1).

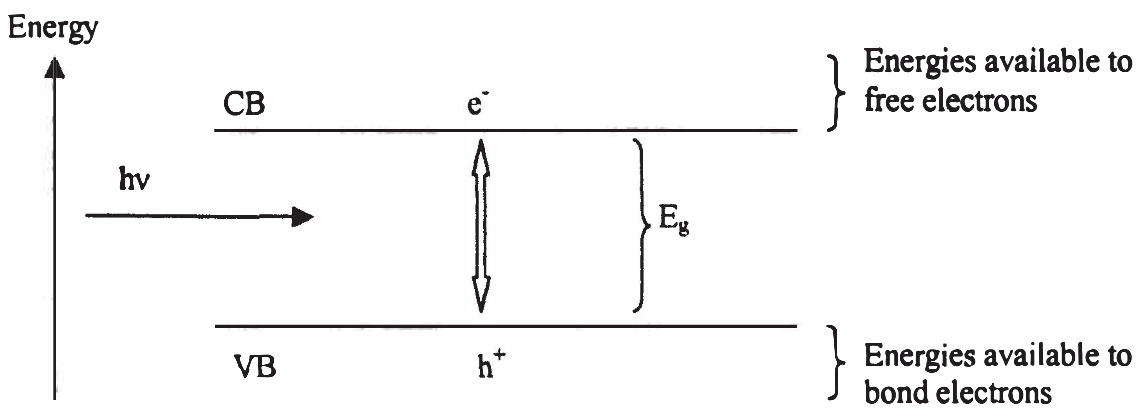

Figure 1.1: The energy diagram for a semiconductor, showing the band gap energy (Nogueira and Wilson, 1993).

The block arrow in Figure 1.1 represents the transition of an electron from VB to CB. Absorption by the particle of photons with energy (hv) greater than the bandgap causes photoexcitation of electron-hole pairs. The band gap energy for TiO_2 is 3.32 eV (Nogueira and Wilson, 1993).

As indicated in Figure 1.2, for many compounds, as the number of monomeric units, N, in a particle increases, the energy necessary to photoexcite the particle decreases. In the limit when $N \geq 2000$, it is possible to end up with a particle which exhibits the band electronic structure of a semiconductor (Mills and Hunte, 1997). As illustrated in Fig. 1.2, in which the highest occupied band (HOMO, the valence band) and lowest unoccupied energy band (LUMO, the conduction band) are separated by a bandgap E_g, a region devoid of energy levels in a perfect crystal.

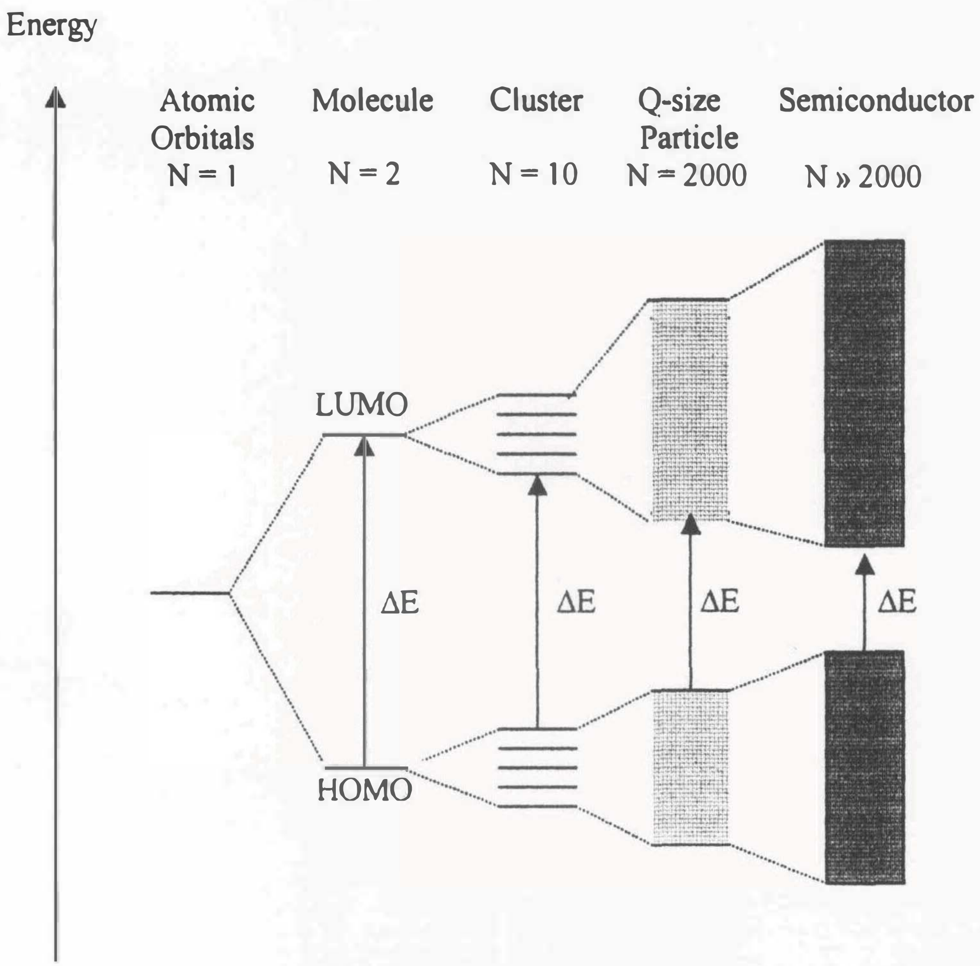

Figure 1.2: Change in the electronic structure of a semiconductor compound as the number N of monomeric units present increase from unity to clusters of more than 2000 (Mills and Hunte, 1997)