UNIVERSITI PUTRA MALAYSIA

ADSORPTION AND PHOTOCATALYTIC PROPERTIES OF IMMOBILISED TITANIUM DIOXIDE-LOADED ACTIVATED CARBON FOR DYE REMOVAL

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By

CHANG SOOK KENG

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

May 2007

Dedicated with much love and affection
to
my parents,
with deep gratitude for all their loving help,
to
my family, who,
by their love and faith in me, have always been a source of great encouragement to me.

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

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Chairman: **Professor Zulkarnain Zainal, PhD**

Faculty: **Science**

With the development of industries and mushrooming of factories venturing into textiles, dyes, pigments, paints and so on, the condition and safety level of water bodies have worsened. Channeling these pollutants into the rivers may lead to unwanted and unsolved environmental problems. Therefore, various methods have been developed to overcome this escalating problem. Activated carbon adsorption is known as a remarkable process due to its large adsorption capacity without forming harmful intermediates or substances while photocatalytic degradation by TiO_2 is a powerful process as it is capable of removing a wide range of organic compounds and achieving a complete mineralization of organics at the end of the process. Combining these two techniques will lead to the enhancement of the removal system.

In this study, adsorption and photocatalytic degradation processes of Methylene Blue were conducted using immobilised mixture of titanium dioxide/activated carbon (TiO_2/AC) under the illumination of ultraviolet (UV) lamp. Immobilised TiO_2/AC was

prepared by applying TiO_2/AC onto a thin layer of PVA/formaldehyde binder that has been spread on glass. The physico-chemical properties of TiO_2/AC were studied by Particle Size Analysis (PSA), Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD), Thermogravimetric Analysis (TGA), Accelerated Surface Area and Porosimetry Analysis (ASAP) and Infrared Analysis (IR). The removal process was studied by varying several parameters such as ball milling of AC in TiO_2/AC, ratio of TiO_2 and AC, suspension loading in the preparation of immobilised TiO_2/AC, initial dye concentration, temperature and light source. The effects of UV light and supply of air towards the removal of cationic dyes: Methylene Blue (MB) and Victoria Blue R (VBR) and anionic dyes: Indigo Carmine (IC) and Naphthol Blue Black (NBB) using immobilised TiO_2, AC and TiO_2/AC were studied in terms of first-order and intraparticle diffusion models. Besides that, isotherm studies were done to determine the adsorption capacity of AC and TiO_2/AC by testing 1000 ppm Methylene Blue using immobilised AC and TiO_2/AC that varies in the number of glasses applied (1-5 glasses).

Immobilised TiO_2/AC showed its best performance under UV illumination with the usage of 1.5 g 30% TiO_2/70% AC. Increasing the dye concentration leads to lower rate constant as the workload of the removal system has increased. The removal of Methylene Blue was an exothermic process. Besides that, immobilised samples containing AC was suitable for the removal of cationic dyes while anionic dyes were better removed by immobilised samples containing TiO_2. The highest rate constants were obtained for these dyes under the illumination of UV light and air supply. The data also fitted well in intraparticle diffusion model. The adsorption capacity of AC and

TiO_2/AC was 370.37 mg/g and 344.83 mg/g respectively. The Langmuir equation gave a better fit to the adsorption isotherm than the Freundlich equation.

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

SIFAT PENJERAPAN DAN FOTOPEMANGKINAN KARBON TERAKTIF TERMUAT-TITANIUM DIOKSIDA YANG DISEKAT GERAK UNTUK PENYINGKIRAN PEWARNA

Oleh

CHANG SOOK KENG

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Pengerusi: **Profesor Zulkarnain Zainal, PhD**

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Pembangunan sektor industri dan pertambahan dalam pembinaan kilang dalam bidang tekstil, pewarna, cat dan sebagainya telah mengakibatkan kemerosotan keadaan dan tahap keselamatan sumber air. Pengaliran bahan pencemar ini ke dalam sungai telah menyebabkan wujudnya masalah-masalah pencemaran alam yang sukar untuk diselesaikan. Dengan ini, pelbagai cara telah dilaksanakan untuk menangani masalah yang semakin ketara ini. Penjerapan karbon teraktif merupakan suatu cara yang baik disebabkan kapasiti penjerapannya yang tinggi tanpa kewujudan bahan perantara atau produk yang bahaya. Proses fotodegradasi dengan titanium dioksida merupakan suatu proses yang berkesan kerana ia dapat menyingkirkan banyak bahan organik dan menukarkan bahan-bahan ini ke bentuk yang tidak bahaya pada akhir proses. Penggabungan dua teknik ini akan meningkatkan kecekapan system penyingkiran.

Dalam kajian ini, proses penjerapan dan fotopemangkinan *Methylene Blue* telah dijalankan dengan menggunakan titanium dioksida/karbon teraktif (TiO_2/AC) tersekat

gerak di bawah penyinaran lampu ultralembayung (UV). TiO_2/AC tersekat gerak disediakan dengan memegunkan TiO_2/AC pada lapisan nipis PVA/formaldehid yang disapukan pada kepingan kaca. Sifat-sifat fizik dan kimia TiO_2/AC dikaji melalui Analisis Saiz Zarah (PSA), Mikroskopi Pengimbasan Elektron (SEM), Pembelauan Sinar-X (XRD), Termogravimetrik (TGA), Luas Permukaan dan Keliangan (ASAP) dan Inframerah (IR). Proses penyingkiran dikaji dengan perubahan beberapa parameter seperti pengisaran bebola pada AC, nisbah TiO_2 dan AC, amaun ampaian dalam penyediaan TiO_2/AC tersekat gerak, kepekatan awal pewarna, suhu dan sumber cahaya. Kesan UV dan bekalan udara terhadap penyingkiran pewarna kationik: *Methylene Blue* (MB) dan *Victoria Blue R* (VBR) dan pewarna anionik: *Indigo Carmine* (IC) dan *Naphthol Blue Black* (NBB) dengan menggunakan TiO_2, AC and TiO_2/AC tersekat gerak dikaji dari segi tertib kinetik pertama dan model penyebaran intrapartikel. Selain itu, kajian isoterma juga dilakukan untuk menentukan kapasiti penjerapan AC dan TiO_2/AC terhadap *Methylene Blue* pada kepekatan 1000 ppm dengan menggunakan bilangan AC dan TiO_2/AC tersekat gerak yang berlainan (1-5 kepingan kaca).

TiO_2/AC tersekat gerak mempamerkan keputusan terbaik dengan penggunaan 1.5 g 30% TiO_2/70% AC di bawah sinaran UV. Pertambahan kepekatan pewarna mengakibatkan penurunan dalam pemalar kadar kerana sistem penyingkiran perlu bekerja dengan lebih kuat. Penyingkiran *Methylene Blue* merupakan proses eksotermik. Selain itu, sampel tersekat gerak yang mengandungi AC adalah lebih sesuai untuk penyingkiran pewarna kationik manakala pewarna anionik lebih sesuai disingkirkan dengan sampel tersekat gerak yang mengandungi TiO_2. Pemalar kadar tertinggi

ditunjukkan oleh pewarna-pewarna ini di bawah penyinaran lampu UV dan bekalan udara. Data juga mematuhi model penyebaran intrapartikel. Muatan penjerapan AC dan TiO_2/AC adalah sebanyak 370.37 mg/g dan 344.83 mg/g masing-masing. Data penjerapan isoterma lebih mematuhi persamaan Langmuir daripada persaman Freundlich.

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I certify that an Examination Committee has met on 21st May 2007 to conduct the final examination of Chang Sook Keng on her Master of Science thesis entitled "Adsorption and Photocatalytic Properties of Immobilised Titanium Dioxide-Loaded Activated Carbon for Dye Removal" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

CHANG SOOK KENG

Date: 18th JUNE 2007

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