



UNIVERSITI PUTRA MALAYSIA

**REMOVAL OF BASIC AND REACTIVE DYES BY SORPTION USING
ETHYLENEDIAMINE-MODIFIED RICE HULL**

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**REMOVAL OF BASIC AND REACTIVE DYES BY SORPTION USING
ETHYLENEDIAMINE-MODIFIED RICE HULL**

By

ONG SIEW TENG

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

July 2006



DEDICATED TO:

My family, Prof. Dr. C. K. Lee, P. S. Keng and friends,
for all that you are and what you mean to me.



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

**REMOVAL OF BASIC AND REACTIVE DYES BY SORPTION USING
ETHYLENEDIAMINE-MODIFIED RICE HULL**

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Chairman: Professor Lee Chnoong Kheng, PhD

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The effectiveness of using ethylenediamine modified rice hull (MRH) to remove Basic Blue 3 (BB3) and Reactive Orange (RO16) from single and binary dye solutions was investigated. The optimised modification process was treating 1.00 g of rice hull with 0.02 mol of ethylenediamine (EDA) in a “well stirred” water bath at 80°C for 2 hours. Surface morphology analysis was carried out using scanning electron microscopy (SEM) and atomic force microscopy (AFM).

Batch and column studies were performed under various experimental conditions and the parameters studied included pH, contact time, initial concentration, temperature, agitation rate, particle size, sorbent dosage, bed depth, flow-rate and sorption –desorption process.

Batch studies reveal that sorption was pH and concentration dependent. The sorption of BB3 and RO16 from single and binary dye solution was found to be



endothermic and exothermic, respectively. The kinetics of dye sorption fitted a pseudo-second order rate expression. Maximum sorption capacities calculated from the Langmuir model are 14.68 and 60.24 mg/g for BB3 and RO16, respectively in binary dye solutions. This corresponds to an enhancement of 4.5 and 2.4 folds, respectively, compared to single dye solutions. The dye uptake increased with increasing sorbent dosage.

Column studies indicate that breakthrough was bed depth, flow rate and influent concentration dependent. Unusual breakthrough curves were obtained for RO16, with very rapid initial breakthrough followed by complete retention at low flow rate, influent concentration and high bed depth. The breakthrough curves of BB3 followed the typical S shape of packed-bed systems. Theoretical breakthrough curves at different bed depths and flow rates generated by the two parameter mathematical model agreed well with the experimental data of single dye solution of BB3. In sorption-desorption process, BB3 can be recovered completely by eluting the column with 0.5 M H₂SO₄ and HCl but the column cannot be reused. However the desorption of RO16 from MRH column was unsuccessful.

The effect of initial concentrations as well as light source was investigated in the photodegradation of BB3 and RO16 using TiO₂ catalyst. Both BB3 and RO16 can be degraded using suspended TiO₂, with either UV or sunlight as the light source.

In the removal of dyes using a combination of sorption and photodegradation, immobilized MRH and TiO₂ were used. The percentage of dye removal increased with increasing irradiation time and the maximum number of dip coatings that can



be applied was ten. MRH dip coated with TiO_2 appeared to be less efficient to remove dyes compared to separate MRH and TiO_2 plates. For all the dye solutions studied, the percentage of dye removal decreased with increasing number of usage of immobilized TiO_2 . Highest percentage of dyes removal was obtained when MRH/ TiO_2 glass plates were placed at a distance of 2.2 cm apart with air bubbling between them.

In the study of treatment of wastewater from textile industry, optimum pH for the sorption of dyes using MRH was in the range of 2 to 5. Uptake of dye under both batch and continuous flow conditions shows similar behavior as in synthetic solutions. However, photodegradation of the dye from the wastewater was unsuccessful.



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

**PENYINGKIRAN PEWARNA BASIK DAN REAKTIF DENGAN ERAPAN
MENGUNAKAN SEKAM PADI TERUBAHSUAI ETILENADIAMINA**

Oleh

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Keberkesanan menggunakan sekam padi terubahsuai etilenadiamina (MRH) untuk menyingkirkan bahan pewarna Basik Biru (BB3) dan Reaktif Oren (RO16) daripada larutan secara berasingan dan gabungan telah dikaji. Keadaan optimum untuk modifikasi telah didapati dengan menindakbalaskan 1.00 g sekam padi dengan 0.02 mol etilenadiamina (EDA) di dalam kukus air pada suhu 80°C dan dikacau selama 2 jam. Analisis morfologi dijalankan dengan menggunakan mikroskopi pengimbasan elektron (SEM) dan mikroskopi daya atomik.

Kajian kelompok dan turus telah dijalankan di bawah pelbagai keadaan eksperimen dan parameter-parameter yang dikaji termasuklah pH, masa kontak, kepekatan awal, suhu, kadar pengacauan, saiz pengerap, dos pengerap, ketinggian turus, kadar aliran dan proses erap-penyaherapan.



Daripada kajian kelompok, keputusan menunjukkan erapan adalah dipengaruhi oleh pH dan kepekatan. Proses erapan BB3 dan RO16 dalam larutan secara berasingan dan gabungan masing-masing adalah endotermik dan eksotermik. Kinetik erapan pewarna adalah mengikut kadar pseudo-kedua. Kapasiti maksimum erapan yang dikira dengan menggunakan model Langmuir bagi BB3 dan RO16 masing-masing adalah 14.68 dan 60.24 mg/g dalam larutan gabungan. Kapasiti maksimum ini merupakan peningkatan sebanyak 4.5 dan 2.4 kali masing-masing berbanding dengan larutan pewarna secara berasingan. Pengambilan pewarna meningkat dengan penambahan dos pengerap.

Kajian turus menunjukkan penembusan adalah bergantung kepada ketinggian turus, kadar aliran dan kepekatan awal. Keluk penembusan yang luarbiasa telah diperolehi bagi RO16 dengan penembusan yang cepat pada peringkat awal dan diikuti dengan penahanan sepenuhnya dalam keadaan kadar aliran perlahan, kepekatan awal rendah dan ketinggian turus panjang. Keluk penembusan bagi larutan secara berasingan BB3 adalah mengikut bentuk tipikal 'S' oleh sistem turus padatan. Keluk penembusan teori yang dihasilkan dengan menggunakan model matematik dua-parameter pada ketinggian turus dan kadar aliran yang berbeza mematuhi data eksperimen bagi larutan secara berasingan BB3. Dalam proses erapan-penyaherapan, BB3 boleh diperolehi semula sepenuhnya dengan menggunakan 0.5 M H₂SO₄ dan HCl sebagai eluen tetapi turus tersebut tidak dapat digunakan semula. Walau bagaimanapun, pewarna RO16 tidak berjaya dinyaherap semula daripada turus MRH.

Kesan kepekatan awal dan juga sumber cahaya telah dijalankan dalam fotodegradasi BB3 dan RO16 menggunakan mangkin TiO_2 . Kedua-dua BB3 dan RO16 boleh difotodegradasikan dengan menggunakan ampaiian TiO_2 dengan UV atau cahaya matahari sebagai sumber cahaya.

Dalam penyingkiran pewarna dengan menggunakan gabungan erapan dan fotodegradasi, MRH dan TiO_2 tergerak-sekat telah digunakan. Peratusan penyingkiran pewarna meningkat dengan penambahan masa sinaran dan bilangan ulangan pencelupan TiO_2 yang boleh diaplikasikan ialah 10 kali. Walau bagaimanapun, MRH yang dicelup dengan TiO_2 adalah kurang berkesan untuk penyingkiran pewarna. Dalam semua larutan pewarna yang dikaji, peratusan penyingkiran pewarna berkurang dengan penambahan bilangan ulangan penggunaan TiO_2 tergerak-sekat. Peratusan tertinggi penyingkiran pewarna diperolehi dengan jarak 2.2 cm antara kepingan kaca MRH/ TiO_2 dengan penggelembungan udara di antaranya.

Dalam kajian perawatan air sisa industri tekstil, pH optimum bagi erapan menggunakan MRH adalah dalam lingkungan 2 hingga 5. Erapan pewarna dari sampel air sisa tekstil dalam kedua-dua kajian kelompok dan turus menunjukkan sifat yang seakan-akan sama seperti dalam larutan sintetik. Tetapi, fotodegradasi bahan pewarna dari air sisa adalah tidak berjaya.

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I certify that an Examination Committee has met on 14 July 2006 to conduct the final examination of Ong Siew Teng on her Doctor of Philosophy thesis entitled “Removal of Basic and Reactive Dyes Using Ethylenediamine Modified Rice Hull and Photodegradation” 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.

ONG SIEW TENG

Date: 1 August 2006



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