UNIVERSITI PUTRA MALAYSIA

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UNIVERSITI PUTRA MALAYSIA

2013

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By

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

May 2013

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

ADSORPTION OF REACTIVE DYES FROM AQUEOUS SOLUTIONS BY QUATERNIZED PALM KERNEL SHELL

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May 2013

Chairman: Intan Salwani Binti Ahamad, PhD

Faculty: Engineering

Quaternized biomass serves as substitution to activated carbon as adsorbent to solve the issue on activated carbon such as cost, environment impact and sustainability. However, there is lack of research on reactive dyes adsorption by quaternized lignocellulosic fibers and none of research on quaternized PKS as adsorbent been reported up to date. Therefore, an attempt was made to chemically quaternized palm kernel shell (QPKS) as adsorbent to increase adsorption affinity towards two reactive dyes namely Reactive Black 5 (RB5) and Reactive Red E (RRE). Palm kernel shell (PKS) was quaternized successfully by treating with N-(3-chloro-2-hydroxypropyl)trimethylammonium chloride under basic condition. The QPKS was characterized by CHN elemental analysis, Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscope (SEM), Energy Dispersive X-Ray (EDX), Brunauer, Emmett and Teller (BET) analysis, Thermalgravimetric analysis (TGA) and X-Ray Diffraction analysis (XRD). Result from CHN and EDX elemental analysis demonstrated an increase of nitrogen percentage after treatment further support the success of the reaction. Surface characterization of QPKS by SEM and

BET analysis confirmed the surface pore enlargement from mesopores to macropores after quaternization. Furthermore, chemical properties such as point zero charge, surface chemistry and chemical composition were determined. Point of zero charge of QPKS measured at 25 ˚C was at pH 2.2.

Adsorption experiment was carried out to investigate the effect of pH, dosage of QPKS, initial concentration, contact time and temperature in single batch system with constant shaking rate of 160 rpm for both dyes. The optimum pH for removal of RB5 and RRE by QPKS was at pH4. 1.0 g/L of QPKS was chosen as the appropriate dosage for both dyes adsorption. Four analytical isotherm equations, Langmuir, Freundlich, Sips and Redlich-Peterson models were fitted to the equilibrium adsorption data. The Redlich-Peterson model is best fitted to the data. The maximum adsorption capacity of QPKS was found to be 191.2 mg/g for RB5 and 182.8 mg/g for RRE. The rate of adsorption in single system was found to agree with pseudo-second-order kinetics model. The adsorption of both dyes onto QPKS is spontaneous process and exothermic in nature. Hence increase in adsorption temperature does not favor the process. For binary system, an artificial neural network (ANN) model was developed to stimulate the adsorption of RB5 and RRE by QPKS under varying parameters such as pH, dosage and dye concentration.

Regeneration of QPKS was carried out by shaking the used QPKS in 0.1M NaOH solution. Regeneration of QPKS for adsorption of RB5 was valid but not for RRE.
In conclusion, the QPKS synthesized was proven able in removing RB5 and RRE dye in aqueous solution.

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

PENJERAPAN PEWARNA REAKTIF DARIPADA LARUTAN AKUES DENGAN MENGGUNAKAN CENGKERANG ISIRONG KELAPA SAWIT YANG TELAH DIKUATERNISASI

Oleh

KOAY YIN SHIN

Mei 2013

Pengerusi: **Intan Salwani Binti Ahamad, PhD**

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Kuartenisasi atas product sampingan industri pertanian mempunyai potensi tinggi untuk menggantikan karbon teraktif sebagai penjerap. Kekurangan penyelidikan terhadap penjerapan pewarna reaktif atas serat kuartenisasi cengkerang isirong kelapa sawit (QPKS) sebagai penjerap sehingga kini. Oleh itu, percubaan telah dilaksanakan untuk mensistesis QPKS sebagai penjerap dengan kaedah kimia, dengan tujuan untuk meningkatkan penjerapan afiniti dua pewarna reaktif, iaitu Reaktif Hitam 5 (RB5) dan Reaktif Merah E (RRE). Cengkerang isirong kelapa sawit (PKS) telah berjaya dikuartenisasi dengan menindak balas dengan N-(3-chloro-2-hydroxypropyl)trimethylammonium chloride dalam keadaan alkali. QPKS telah diciri dengan menggunakan analisai unsur CHN, Spektroskopi Inframerah Transformasi Fourier (FTIR), Pengimbas Mikroskop Elektron (SEM), Penyebar Tenaga X-Ray (EDX), analisasi Brunauer, Emmett dan Teller (BET),Thermogravimetrik analisasi (TGA), dan analisasi X-Ray Pembelauan (XRD). Di samping itu, analisis unsur CHN dan EDX menunjukkan peningkatan

peratusan nitrogen pada QPKS selepas ditindak balas menjadi sokongan yang kukuh bahawa tindak balas kuartenisasi telah berjaya. Selain itu, pencirian permukaan QPKS oleh SEM dan BET analisasi mengesahkan pembesaran liang permukaan dari meso kepada macro selepas pengubahsuaian. Tambahan pula, sifat-sifat kimia seperti titik caj kosong, kimia permukaan, dan komposisi kimia telah ditentukan. Titik caj sifar QPKS yang diambil bacaan pada suhu 25 ˚C adalah di pH 2.2.

Kajian penjerapan telah dijalankan untuk mengaji kesan pH, dos QPKS, kepekatan awal pewarna reaktif, masa reaksi, dan kesan suhu dalam sistem kelompok dengan kadar goncangan 160 rpm. pH optima untuk penyingkiran RB5 dan RRE oleh QPKS adalah pada pH 4. 1.0 g/L dos QPKS telah ditentukan sebagai jumlah m ńimum yang diperlukan dengan menunjukkan penyingkiran yang terbaik untuk kedua-dua pewarna. Equilibria isoterm dianalisis oleh model Langmuir, Freundlich, Sips, dan Redlich-Peterson dan Redlich-Peterson model paling menghampiri data-data kajian. Kapasiti maximum penjerapan MPKS didapati ialah 191 mg/g untuk RB5 dan 182 mg/g untuk RRE. Kadar penjerapan dalam sistem tunggal didapati setuju dengan kinetik pseudo-tertib kedua. Untuk sistem binari, model penjerapan RB5 dan RRE oleh MPKS bawah parameter yang berbeza seperti pH, dos MPKS, dan kepekatan pewarna telah mensimulasikan dengan menggunakan rangkaian neural tiruan (ANN). Penjerapan kedua-dua pewarna pada QPKS adalah reaksi spontan dan eksotermik.

Penjanaan QPKS telah dilaksanakan dengan mengoncang QPKS yang terpakai dalam 0.1M NaOH. MPKS gagal dijana semula untuk penjerapan RRE tetapi boleh diguna pakai semula untuk penjerapan RB5. Kesimpulannya, penjerap QPKS yang disintisis dibuktikan cekap dalam menjerap RB5 dan RRE pewarna.

ACKNOWLEDGEMENTS

I would like to express my utmost gratitude to my supervisor Dr.Intan Salwani Binti Ahamad and co-supervisors Prof. Luqman Chuah Abdullah Prof. Thomas Choong Shean Yaw and Dr. Mohsen for their valuable guidance, support and constructive comments throughout this project. I would like to gratefully acknowledge the technicians in the Department of Chemical and Environmental Engineering and my colleagues for their willingness in helping me. A Loving thanks to my family and friends who give me encouragement and support throughout this journey. From the deepest of my heart, I am very grateful and appreciate to all individual who had contributed in my work. Sincere apologies to any individual I had unintentionally left off.

I certify that a Thesis Examination Committee has met on May 2013 to conduct the final examination of Koay Yin Shin on her Master of Science thesis entitled "Adsorption of Reactive Dyes from Aqueous Solutions by Modified Palm Kernel Shell" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the degree of Master of Science.

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This thesis submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

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DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or other institution.

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KOAY YIN SHIN

Date: 20 May 2013

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