PREPARATION AND CHARACTERIZATION OF MICROWAVE-MODIFIED ADSORBENTS FROM *Casuarina equisetifolia* SEEDS FOR DYE ADSORPTION APPLICATION

ANIS AYUNI BINTI AMAN ZUKI

MASTER OF SCIENCE
UNIVERSITI MALAYSIA TERENGGANU
2016

ANIS AYUNI BINTI AMAN ZUKI

MASTER OF SCIENCE

2016

PREPARATION AND CHARACTERIZATION OF MICROWAVE-MODIFIED ADSORBENTS FROM *Casuarina equisetifolia* SEEDS FOR DYE ADSORPTION APPLICATION

ANIS AYUNI BINTI AMAN ZUKI

MASTER OF SCIENCE

UNIVERSITI MALAYSIA TERENGGANU

2016

PREPARATION AND CHARACTERIZATION OF MICROWAVE-MODIFIED ADSORBENTS FROM *Casuarina equisetifolia* SEEDS FOR DYE ADSORPTION APPLICATION

ANIS AYUNI BINTI AMAN ZUKI

Thesis Submitted in Fulfillment of the Requirement for the Degree of Master of Science in the School of Ocean Engineering Universiti Malaysia Terengganu

2016

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

PREPARATION AND CHARACTERIZATION OF MICROWAVE-MODIFIED ADSORBENTS FROM *Casuarina equisetifolia* SEEDS FOR DYE ADSORPTION APPLICATION

ANIS AYUNI BINTI AMAN ZUKI

November 2016

Main Supervisor : Associate Professor Dr. Mohamad Bin Awang, Ph.D.

Co-Supervisor : Dr. Asmadi Bin Ali @ Mahmud, Ph.D.

School : School of Ocean Engineering

Nowadays, numerous approaches have been focused for the development of cheaper, effective and environment friendly adsorbents as alternatives to replace activated carbon and other adsorbents. In this study, raw *Casuariana equisetifolia* seeds and p-toluene sulfonic acid as well as sodium hydroxide (NaOH) treated seeds with and without microwave treatment were used as adsorbents for the malachite green (MG) and neutral red (NR) dye removal. The treated adsorbents were prepared by soaking the seeds in the p-toluene sulfonic acid and NaOH. The microwave-modified adsorbents were prepared by treating the seeds in the microwave oven with the frequency of 2.34 GHz, 800 W and 8 min irradiation time before the seeds were treated with the p-toluene sulfonic acid and NaOH. The adsorbents were characterized based on the chemical characteristic, physical characteristics and surface morphological. The batch adsorption experiments were performed for the removal of MG and NR dyes. The results reveal that microwave-acid-alkali treated *C. equisetifolia* seeds have the lowest ethanol-toluene solubility and hot water solubility that determine the quantity of extraneous materials compared raw and acid-alkali treated seeds. The lowest value of extraneous materials led to increase the active surface of adsorbent and thus

promote the adsorption efficiency. Besides that, the content of lignocellulose materials of adsorbent showed higher values that can promote the binding of dyes. The FTIR spectra of microwave-acid-alkali treated seeds have high intensity of C-H stretch, C=O stretch and C-O groups at band 2924 cm^{-1}, 1701-1720 cm^{-1} and 1022-1026 cm^{-1}, respectively, which can enhance the adsorption capacity of adsorbents. Besides, the micrographs of adsorbents show that the surface of the microwave-acid-alkali treated seeds was full of cavities and cracks as compared to that of raw and acid-alkali treated seeds. Surface charge of the adsorbents show negative zeta potential values which is related to the negatively charge ion of carboxyl and phenolic OH groups that can promote the binding of cationic dyes. The equilibrium adsorption for all batch adsorption experiments was achieved within 150 min. The highest percentage of MG and NR dye removal for microwave-acid-alkali treated seeds was achieved at 1.0 g/100 mL of 200 mg/L of dye which are 95.96 and 97.24 %, respectively. Equilibrium data were best presented by Langmuir model with high correlation coefficient 0.984 to 0.999 representing the adsorption of dye was taken place at specific homogeneous sites of adsorbents. Meanwhile, for kinetic study, the adsorption process followed pseudo-second-order kinetic model with correlation coefficient between 0.7932 and 0.9980 for both dyes indicating the chemisorption has occurred between adsorbents and dye molecules.

Abstrak thesis yang dikemukakan kepada Senat Universiti Malaysia Terengganu sebagai memenuhi keperluan untuk Ijazah Sarjana Sains

PENYEDIAAN DAN PENCIRIAN PENJERAP DIUBAHSUAI OLEH GELOMBANG MICRO DARI BIJI *Casuarina equisetifolia* UNTUK PENGGUNAAN PENJERAPAN PEWARNA

ANIS AYUNI BINTI AMAN ZUKI

November 2016

Penyelia Utama : Profesor Madya Dr. Mohamad Bin Awang, Ph.D.

Penyelia Bersama : Dr. Asmadi Bin Ali @ Mahmud, Ph.D.

Pusat Pengajian : Pusat Pengajian Kejuruteraan Kelautan

Masa kini, pelbagai pendekatan telah diberi tumpuan untuk penghasilan penjerap yang murah, berkesan dan mesra alam sebagai alternatif untuk menggantikan karbon diaktifkan dan penjerap lain. Dalam kajian ini, biji *Casuariana equisetifolia* tidak dirawat dan biji dirawat dengan asid p-toluena sulfonik serta natrium hidroksida (NaOH) bersama dan tanpa rawatan gelombang mikro digunakan sebagai penjerap untuk menyingkiran hijau malachite (MG) dan merah neutral (NR). Penjerap yang dirawat disediakan dengan merendam biji di dalam asid p-toluna sulfonik dan NaOH. Penjerap diubah suai dengan gelombang mikro dirawat di dalam ketuhar gelombang mikro dengan frekuensi 2.34 GHz, 800 W dan 8 min masa penyinaran sebelum dirawat dengan asid p-toluena sulfonik dan NaOH. Pencirian penjerap dibuat berdasarkan sifat kimia, sifat fizikal dan morfologi permukaan. Penjerap dikaji dalam eksperimen penjerapan kelompok untuk menyingkirkan pewarna MG dan NR. Keputusan menunjukkan biji *C. equisetifolia* dirawat gelombang mikro-asid-alkali mempunyai kelarutan etanol-toluena dan air panas terendah yang menunjukkan kuantiti bahan luaran berbanding dengan biji tidak dirawat dan dirawat oleh asid-alkali. Nilai kandungan bahan luaran yang rendah dapat meningkatkan permukaan aktif pada

penjerap dan seterusnya meningkatkan kecekapan penjerapan. Selain itu, bahan lignoselulosa bagi penjerap menunjukkan nilai tinggi dapat membantu ikatan pewarna. Spektrum FTIR bagi biji dirawat gelombang mikro-asid-alkali mempunyai intensiti yang lebih tinggi pada regangan C-H , ikatan C=O dan kumpulan C-O pada lingkaran 2924 cm^{-1}, 1701-1720 cm^{-1} dan 1022-1026 cm^{-1} yang boleh meningkatkan kapasiti penjerapan. Selain itu, mikrograf penjerap menunjukkan permukaan biji dirawat mikro-asid-alkali mempunyai rongga dan keretakan berbanding biji tidak dirawat dan dirawat asid-alkali. Cas permukaan penjerap menunjukkan nilai negatif bagi potensi zeta yang berkaitan ion bercas negatif pada kumpulan OH karboksil dan fenolik yang boleh menggalakkan mengikatan pewarna kationik. Keseimbangan penjerapan bagi semua eksperimen penjerapan kelompok telah dicapai dalam tempoh 150 minit. Peratusan penyingkiran tertinggi pewarna MG dan NR untuk biji dirawat mikro-asid-alkali adalah pada 1.0 g/100 mL bagi 200 mg/L kepekatan iaitu masing-masing 95.96 dan 97.24%. Data keseimbangan yang terbaik ditunjukkan oleh model Langmuir dengan pekali korelasi yang tinggi iaitu 0.984-0.999 menunjukkan penjerapan pewarna berlaku pada laman homogen tertentu pada penjerap. Sementara itu, untuk kajian kinetik, proses penjerapan mengikuti model kinetik pseudo-kedua dengan pekali korelasi antara 0.7932 dan 0.9980 untuk kedua-dua pewarna yang menunjukkan penjerapan kimia telah berlaku antara penjerap dan molekul pewarna.