



UNIVERSITI PUTRA MALAYSIA

**REMOVAL OF CHROMIUM(VI), COPPER(II) AND ARSENIC(V) FROM
AQUEOUS SOLUTION AND WASTEWATER BY ETHYLENEDIAMINE
MODIFIED RICE HULL**

TANG POH LI

FSAS 2002 20

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MODIFIED RICE HULL**

By

TANG POH LI

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

February 2002



DEDICATED TO:

My family, supervisory committee and friends,

for the support and encouragement

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

**REMOVAL OF CHROMIUM(VI), COPPER(II) AND ARSENIC(V) FROM
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February 2002

Chairman : Prof. Dr. Lee Chnoong Kheng, Ph.D.

Faculty : Science and Environmental Studies

The potential of aminated rice hull to remove Cr(VI), Cu(II) and As(V) from aqueous solution was investigated. Amination processes enhanced the sorption capacities of rice hull with ethylenediamine being the most economical and efficient aminating agent. Chemical modification of surface functional groups of ethylenediamine modified rice hull (enRH) indicated that amine and carboxyl groups were the major sorption sites.

Both batch and column studies were performed, taking into account parameters such as pH, contact time, initial concentrations, ionic strength, particle size of sorbent, rate of agitation, presence of competitive cation and anions, use of different metal ion sources, sorbent dosage, temperature, bed depth, flow rate and sorption-desorption process.

The results of batch studies indicated that the sorption process was pH and temperature dependent. External mass transfer was not the sole rate-limiting phase and might involve chemisorption. The sorption of metal ions from single metal ion solution was in the order of $\text{Cr(VI)} > \text{Cu(II)} > \text{As(V)}$ which is consistent with the Pearson's theory on hard and soft acid base. Cr(VI) and As(V) sorptions involved electrostatic interactions while Cu(II) sorption involved complexation. Where Cu(II) was present in binary and ternary metal ion solutions, Cr(VI) and As(V) removal also involved complexation.

Column studies revealed different equilibrium states compared with batch studies. Breakthrough was bed depth, flow rate and initial concentration dependent. The presence of sulfate significantly affected the breakthrough time of Cr(VI) and Cu(II). The relationship between service time and bed depth was linear. The predicted breakthrough curves obtained from a two-parameter mathematical model agreed well with the experimental values in Cu(II) from all systems and Cr(VI) from binary Cu(II)-Cr(VI) and ternary metal ion solutions when sulfate was absent.

Sequential columns could successfully reduce the levels of Cr(VI) and Cu(II) in the wastewater to the allowable limit for discharge into inland water. Cr(VI) and Cu(II) from dilute solution could be preconcentrated on the enRH column and thus this is useful in the analysis of trace amounts of Cr(VI) and Cu(II) in wastewater. Elution of Cr(VI)- and Cu(II)-loaded column could be carried out using 1.07 M NH_3 and 0.5 M H_2SO_4 , respectively.

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

**PENYINGKIRAN KROMIUM(VI), KUPRUM(II) DAN ARSENIK(V)
DARIPADA LARUTAN AKUEUS DAN AIR SISA OLEH SEKAM PADI
YANG DIUBAHSUAIKAN DENGAN ETILENADIAMINA**

Oleh

TANG POH LI

Februari 2002

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Keupayaan sekam padi (NRH) yang diaminakan untuk penyingkiran Cr(VI), Cu(II) dan As(V) dari larutan akueus telah dikaji. Proses pengaminaan telah meningkatkan kapasiti erapan sekam padi. Etilenadiamina merupakan agen amina yang paling ekonomi dan berkesan. Pengubahsuaian kimia ke atas kumpulan-kumpulan berfungsi pada sekam padi terubahsuai oleh etilenadiamina (enRH) menunjukkan bahawa kumpulan amina dan karboksilik merupakan tapak erapan utama.

Kajian kelompok dan turus telah dijalankan dengan mengambilkira parameter-parameter seperti pH, masa kontak, kepekatan awal, kekuatan ion, saiz pengeras, kadar pengacauan, kehadiran kation dan anion-anion pesaing, penggunaan sumber logam berbeza, suhu, ketinggian turus, kadar aliran and edaran erapan-nyaherpan.

Kajian kelompok menunjukkan bahawa proses erapan dipengaruhi oleh pH dan suhu. Pemindahan jisim luar bukan langkah penentu kadar tunggal dan melibatkan erapan kimia. Erapan logam-logam daripada larutan logam tunggal berurutan $\text{Cr(VI)} > \text{Cu(II)} > \text{As(V)}$ selaras dengan teori Pearson mengenai asid dan bes liat dan lembut. Erapan Cr(VI) dan As(V) melibatkan interaksi elektrostatik manakala erapan Cu(II) melibatkan pembentukan kompleks. Di mana Cu(II) hadir, penyingkiran Cr(VI) dan As(V) juga melibatkan pembentukan kompleks.

Kajian turus memaparkan perbezaan di antara keadaan keseimbangan dengan kajian kelompok. Penembusan bergantung kepada tinggi turus, kadar aliran dan kepekatan awal. Kehadiran sulfat telah mempengaruhi masa penembusan Cr(VI) dan Cu(II) . Hubungan di antara masa khidmat dan tinggi turus adalah linear. Keluk penembusan ramalan menggunakan model matematik dua-parameter mematuhi nilai eksperimen bagi Cu(II) dari larutan logam tunggal dan Cr(VI) dari larutan Cu(II) - Cr(VI) dan ternari yang tidak dihadiri sulfat.

Turus berganda dapat mengurangkan Cr(VI) dan Cu(II) di dalam air sisa sehingga takat yang dibenarkan untuk disingkirkan. Cr(VI) dan Cu(II) daripada larutan cair dapat dipekatkan pada enRH dan dengan demikian berguna untuk analisis Cr(VI) dan Cu(II) yang berkepekatan rendah dalam air sisa. Elusi turus yang ditepuan oleh Cr(VI) dan Cu(II) masing-masing dilakukan dengan menggunakan 1.07 M larutan NH_3 dan 0.5 M H_2SO_4 .

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I certify that an Examination Committee met on 22nd February 2002 to conduct the final examination of Tang Poh Li on her Doctor of Philosophy of Science thesis entitled "Removal of Chromium(VI), Copper(II) and Arsenic(V) from Aqueous Solution and Wastewater by Ethylenediamine Modified Rice Hull" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulation 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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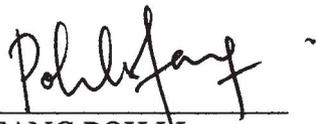


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DECLARATION

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 degree at UPM or other institutions.


TANG POH LI

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