SORPTION OF CHROMIUM(VI) AND COPPER(II) FROM AQUEOUS SOLUTION BY CHEMICALLY-MODIFIED RICE HULL

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

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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

SORPTION OF CHROMIUM(VI) AND COPPER(II) FROM AQUEOUS SOLUTION BY CHEMICALLY-MODIFIED RICE HULL

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Chairman : Professor Lee Chnoong Kheng, Ph.D.

Faculty : Science and Environmental Studies

The sorption of Cr(VI) and Cu(II) from single and binary metal solutions by rice hull modified using different chemical reagents were investigated. Modification of rice hull using citric acid and quaternary ammonium salt was investigated and optimized to yield a material (citric acid-quaternized rice hull – CQRH) which was capable of removing both Cr(VI) and Cu(II) simultaneously and efficiently.

Batch and column studies were carried out in order to understand the sorption characteristic of Cr(VI) and Cu(II) by CQRH. The parameters studied were pH, contact time, agitation rate, initial concentration of metal solutions, presence of other cations and chelators, competitive cation and anion, particle size, bed depth, flow rate and sorption-desorption cycles using synthetic solution and electroplating wastewater.

In batch studies, sorption was pH dependent and equilibrium was attained in less than 30 minutes. Kinetic study showed that sorption followed the pseudo-second order kinetics. The sorption of Cr(VI) from single and binary metal ion solutions was found to be an exothermic and endothermic process, respectively while sorption of Cu(II) was an endothermic process. For single metal ion solution, the sorption process conformed to the Langmuir isotherm with maximum sorption capacities of 0.46 and 0.12 mmol/g at 28±2^{o}C for Cr(VI) and Cu(II), respectively. For binary metal ion solution, sorption capacity of Cr(VI) was 0.53 mmol/g while that of Cu(II) was similar to that in single metal solution. In the presence of chelators, metal uptake decreased and the uptake of Cr(VI) and Cu(II) were not affected by agitation rate and particle size.

The results of column studies showed that breakthrough depended on bed depth and initial concentration of metal ion. However, sorption was flow rate independent. Predicted breakthrough curves obtained from two parameter mathematical model agreed well with experimental values for Cr(VI) from binary metal ion solution and Cu(II) from single and binary metal ion solutions. For Cr(VI) from single metal ion solution, predicted breakthrough curves obtained from two parameter mathematical model did not agree well with experimental values. In sorption-desorption study, Cr(VI) and Cu(II) could be removed effectively by eluting with 0.05 M NaOH and H_2SO_4, respectively. Sorption-desorption process for Cr(VI)-CQRH system can be repeated for at least 5 cycles without deterioration capability of CQRH while in the case of Cu(II)-CQRH system, it could only be used once.

In the case of wastewater, the poor capability of CQRH to remove Cr(VI) from electroplating wastewater under continuous flow conditions could be due to the wastewater containing other anionic species such as SO_4^{2-} and PO_4^{3-}. Besides that sorption of Cr(VI) from electroplating wastewater needed longer time to reach equilibrium compared to synthetic solution which may affect the uptake of Cr(VI) in column study.

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

ERAPAN KROMIUM(VI) DAN KUPRUM(II) DARIPADA LARUTAN AKUEUS OLEH SEKAM PADI YANG DIUBAHSUAI DENGAN AGEN BAHAN KIMIA

Oleh

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Erapan Cr(VI) dan Cu(II) dari larutan logam tunggal dan binari oleh sekam padi yang diubahsuai telah dikaji. Pengubahsuaian sekam padi dengan asid sitrik dan garam kuaternari ammonium telah dikaji dan dioptimumkan untuk menghasilkan satu bahan (CQRH) yang mampu untuk menyingkirkan Cr(VI) dan Cu(II) dengan serentak dan berkesan.

Kajian kelompok dan turus telah dijalankan untuk memahami ciri-ciri erapan CQRH terhadap Cr(VI) dan Cu(II). Parameter-parameter yang telah dikaji adalah seperti pH, masa kontak, kadar acuman, kepekatan awal, kehadiran kation dan agen pengkelat, kehadiran kation dan anion pesaing, saiz zarah, ketinggian turus, kadar aliran dan edaran erapan-penyaherapan dengan menggunakan larutan sintetik dan air sisa saduran.

Dalam kajian kelompok, proses erapan dipengaruhi oleh pH dan keseimbangan tindak balas dicapai kurang daripada 30 minit. Kajian kinetik menunjukkan proses erapan merupakan proses tertib tindak balas pseudo kedua. Proses erapan untuk Cr(VI) daripada larutan logam tunggal dan larutan Cr(VI)-Cu(II) masing-masing merupakan proses eksotermik dan endotermik. Untuk Cu(II), proses erapan adalah proses endotermik. Untuk larutan logam tunggal, kapasiti erapan maksimum untuk Cr(VI) dan Cu(II) pada suhu 28±2^{o}C yang ditentukan daripada isoterma Langmuir masing-masing adalah 0.46 and 0.12 mmol/g. Untuk larutan Cr(VI)-Cu(II), kapasiti erapan maksimum untuk Cr(VI) adalah 0.53 mmol/g manakala kapasiti erapan maksimum untuk Cu(II) adalah sama seperti dalam larutan logam tunggal. Dalam kehadiran agen pengkelat, kadar erapan logam berkurang dan kadar erapan untuk Cr(VI) dan Cu(II) tidak dipengaruhi oleh kadar acuman dan saiz zarah.

Keputusan kajian turus menunjukkan kadar kemunculan bergantung pada tinggi turus dan kepekatan awal, tetapi tidak dipengaruhi oleh kadar aliran. Keluk kemunculan ramalan menggunakan model matematik dua-parameter mematuhi nilai eksperimen bagi Cr(VI) daripada larutan Cr(VI)-Cu(II) dan Cu(II) daripada kedua-dua larutan. Bagi Cr(VI) daripada larutan logam tunggal, keluk kemunculan ramalan tidak mematuhi nilai eksperimen. Dalam kajian erapan-penyaherapan, Cr(VI) dan Cu(II) masing-masing dapat dielusi dengan larutan 0.05 M NaOH and H_2SO_4. Untuk sistem Cr(VI)-CQRH, proses erapan-penyaherapan dapat dilakukan sekurang-kurangnya 5 kitaran manakala proses erapan-penyaherapan untuk sistem Cu(II)-CQRH hanya boleh dilakukan sekali sahaja.

Dalam kajian turus untuk air sisa saduran, CQRH menunjukkan kadar penyingkiran Cr(VI) yang tidak memuaskan. Ini mungkin disebabkan oleh kehadiran spesis anionik yang lain seperti SO_4^{2-} and PO_4^{3-}. Selain itu, erapan untuk Cr(VI) daripada air sisa saduran memerlukan masa yang lebih lama untuk mencapai keseimbangan jika dibandingkan dengan larutan sintetik.

I certify that an Examination Committee met on 2nd September 2004 to conduct the final examination of Tan Hong Sun on his degree of Master of Science thesis entitled "Sorption of Cr(VI) and Cu(II) by Chemically-Modified Rice Hull" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committees 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 currently submitted for any other degree at UPM or other institutions.

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