UNIVERSITI PUTRA MALAYSIA

BIOLEACHING AND BIOSORPTION OF HEAVY METALS FROM GOLD MINE TAILINGS BY *ASPERGILLUS FUMIGATUS* IN PENJOM, MALAYSIA

BAHI JALILI SEH BARDAN

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By

BAHI JALILI SEH BARDAN

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

January 2012

DEDICATION

This work is dedicated to:

My husband, Fardin, for his endless patience and encouragement.

My father, Amir, who is a true scholar, my favorite storyteller, and always encourages my interests in science.

My mother, Ameneh, whose love, nurturing, and motivation during my graduate career were invaluable, and who I always admire for her endless energy.

My sisters, brothers, sister-in-law and brothers-in-law for their understanding and love that has supported me throughout the various challenging and rewarding experiences of my life.

My wonderful nephew, Ahura, who changed my life when he was born.

My best friend, Mahtab, for her sisterly moral support.

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

BIOLEACHING AND BIOSORPTION OF HEAVY METALS FROM GOLD MINE TAILINGS BY *ASPERGILLUS FUMIGATUS* IN PENJOM, MALAYSIA

By

BAHI JALILI SHE BARDAN

January 2012

Chairman: Radziah Othman, PhD

Faculty: Agriculture

Mine tailings is an important source of heavy metal contamination in the environment. Decontamination of the mine tailings is necessary for the protection of the environment. In recent years, bioleaching process has gained increasing attention for extraction of metals from solid substrate, since it is simple, environmentally friendly and economical. The objectives of this study were (i) to characterize some physicochemical properties of gold mine tailings and to isolate and identify indigenous fungi from the tailings, (ii) to evaluate the ability of the indigenous fungus to bioleach heavy metals in step bioleaching and column bioleaching processes using distributed and surface applied techniques, and (iii) to assess the efficiency of *A. fumigatus* biomass to biosorb and remove metal from synthetic solutions and from leachate

derived from a gold mine. Bioleaching experiments were conducted for the removal of heavy metals from mine tailings using a fungal strain isolated from the gold mine tailings and it was identified as *A. fumigatus* based on its 18S rDNA analysis. The bioleaching processes were carried out in one-step and spent medium leaching at 1%, 2%, 4% and 8% (w/v) tailing concentrations. Column bioleaching experiments were carried out to compare the effectiveness of the fungus to bioleach heavy metals from the tailings using distribution technique (DT) and surfaced applied technique (SAT). The ability of *A. fumigatus* to remove As, Fe, Mn, Pb and Zn from synthetic solutions and from leachate derived from gold mine during bioleaching was assessed. Batch sorption experiments were carried out to characterize the capability of fungal biomass (FB) and iron-coated fungal biomass (ICFB) to remove metal ions in single and multi-solute systems. Results showed that in the one step bioleaching process, production of oxalic acid was the highest among the other organic acids; while in the spent medium leaching citric acid was dominant. The removal of As, Fe, Mn and Zn was higher in the one step than the spent medium leaching but the reverse was observed for Pb. Heavy metals removal efficiency decreased with increasing concentration of tailings in both bioleaching processes. The column bioleaching study showed that DT produced higher oxalic acid than the SAT, therefore more As, Fe, Mn, and Zn were removed by the DT method compared to the SAT. However, Pb removal was low by DT than the SAT probably due to the precipitation of Pb as its oxalates. The DT was a more promising method for removal of metal

ions from the mine tailings because distributing the fungus throughout the entire soil column improved the bioleaching efficacy of the heavy metals. The biosorption study showed that sorption data for all systems fitted well the Langmuir isotherm equation. The maximum sorption capacities of metals by both FB and ICFB were higher in the single metal system than the multi-solute system. It indicates that the presence of multiple metal ions in as solution suppressed adsorption of the individual metal ions. Sorption capacity of ICFB was higher than FB for all metal ions because the net surface charge of ICFB was more negative than FB at the pH range of 6 to 9, therefore the ICFB could adsorb more cationic metals. As for As adsorption, the As formed complexes with the Fe oxide of the ICFB surface sites. The FT-IR analysis showed that the functional groups of the fungal biomass were involved in the metal ions sorption. Overall, the results suggest that bioremediation process using *A. fumigatus* was effective for the leaching of heavy metals from mine tailings especially in the one-step bioleaching process using the DT method. The ICFB was found to be effective in adsorbing the metals present in the leachate of the tailing bioleaching process.

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

BIOLURUHLARUTAN DAN BIOJERAPAN LOGAM BERAT DARIPADA SISA LOMBONG EMAS OLEH *ASPERGILLUS FUMIGATUS* DALAM PENJOM, MALAYSIA

Oleh

BAHI JALILI SEHBARDAN

Januari 2012

Pengerusi: Radziah Othman, PhD

Fakulti: Pertanian

Tahi lombong adalah punca penting pencemaran logam berat dalam persekitaran. Dekontaminasi tahi lombong adalah perlu bagi perlindungan alam sekitar. Pada tahun-tahun kebelakangan ini, proses larutlesap telah mendapat perhatian yang semakin meningkat bagi pengekstrakan logam daripada substrat pepejal, kerana ia mudah, mesra alam dan ekonomi. Objektif kajian ini adalah (i) untuk mencirikan beberapa sifat tahi lombong emas dan untuk mengasingkan dan mengenal pasti kulat asli dari tahi lombong tersebut, (ii) untuk menilai kemampuan kulat asli *A. fumigatus* untuk melarutlesapbio logam berat dalam proses larutlesapbio di dalam kolum menggunalan teknik edaran dan teknik taburan pada permukaan, dan (iii) untuk menilai keberkesanan biojisim *A. fumigatus* untuk menjerapbio dan

mengeluarkan ion logam dalam air yang terhasil dari proses larutlesapbio.Eksperimen larutlesapbio telah dijalankan untuk penyingkiran logam berat dari tahi lombong dengan menggunakan strain kulat yang diasingkan daripada tahi lombong emas dan ia telah dikenal pasti sebagai *A. fumigatus* berdasarkan analisis 18S rDNA. Proses larutlesapbio telah dijalankan dalam satu langkah, dengan kepekatan media tahi lombong pada kepekatan 1%, 2%, 4% dan 8% (w / v).Eksperimen larutlesapbio lajur dijalankan untuk membandingkan keberkesanan kulat untuk menglarutlesapbiologam berat daripada tahi lombong menggunakan teknik pengagihan (TP) dan teknik taburan permukaan (TTP). Keupayaan *A. fumigatus* untuk menghapuskan As, Fe, Mn, Pb dan Zn daripada larutan sintetik dan daripada hasil larutlesap yang berasal dari lombong emas semasa larutlesapbio dinilai. Eksperimen jerapan sekumpulan telah dijalankan untuk mencirikan keupayaan biojisim kulat (BK) dan biojisim ferum bersalut kulat (BFBK) untuk mengeluarkan ion logam dalam sistem tunggal dan pelbagai bahan larut.Hasil kajian menunjukkan bahawa dalam proses larutlesapbio satu langkah, pengeluaran asid oksalik adalah yang tertinggi di kalangan asid organik yang lain, sedangkan dalam medium hasil larut lesap, asid sitrik adalah dominan. Penyingkiran As, Fe, Mn dan Zn adalah lebih tinggi dalam proses langkah salah satu daripada medium hasil larut lesap tetapi sebaliknya dilihat untuk Pb. Kecekapan penyingkiran logam berat menurun dengan peningkatam kepekatan tahi lombong di kedua-dua proses larutlesapbio. Kajian larutlesapbio kolum menunjukkan TP menghasilkan asid

oksalik yang lebih tinggi daripada TTP, oleh itu, lebih banyak As, Fe, Mn, dan Zn telah dikeluarkan dengan kaedah DT berbanding SAT. Walau bagaimanapun, penyingkiran Pb adalah rendah oleh TP berbanding TTP mungkin disebabkan oleh pemendakan Pb sebagai oksalat. Kaedah TP adalah lebih berpotensi untuk penyingkiran ion logam daripada tahi lombong kerana agihan kulat sepanjang kolum tanah meningkatkan keberkesanan larutlesapbio logam berat. Kajian biojerapan menunjukkan bahawa data jerapan untuk semua sistem dilengkapi boleh disesuaikan dengan persamaan isotherma Langmuir. Kapasiti maksima jerapan logam oleh kedua-dua BK dan BFBK dalam sistem logam tunggal adalah lebih tinggi daripada sistem pelbagai bahan larut. Ia menunjukkan bahawa kehadiran pelbagai ion logam menekan penjerapan penjerapan ion logam secara individu. Kapasiti jerapan BFBK adalah lebih tinggi daripada BK untuk semua ion logam kerana caj bersih permukaan BFBK adalah lebih negatif daripada BK pada julat pH 6-9, oleh itu BFBKB boleh menjerap logam yang lebih kationik. Bagi penjerapan As, ia membentuk kompleks dengan oksida Fe pada permukaan BFBK. Analisa FT-IR menunjukkan bahawa kumpulan berfungsi biojisim kulat terlibat dalam jerapan ion logam.Secara keseluruhan, keputusan menunjukkan bahawa proses bioremediasi menggunakan *A. fumigatus* berkesan untuk larutlesap logam berat dari tahi lombong terutamanya dalam proses larutlesapbio satu langkah menggunakan kaedah TP. BFBK didapati berkesan dalam menjerap logam yang hadir dalam hasil larutlesap proses larutlesapbio tahi lombong.

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I certify that a Thesis Examination Committee has met on 5 January 2012 to conduct the final examination of Bahi Jalili Seh Bardan on his Doctor of Philosophy thesis entitled "Bioleaching and biosorption of heavy Metals from gold mine tailings in Penjom, Malaysia, by *Aspergillus fumigatus*" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U. (A) 106] 15th March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.
Members of the Thesis Examination Committee were as follows:

Shamsuddin Jusop, PhD
Professor
Faculty of Agriculture
Universiti Putra Malaysia
(Chairman)

Sariah Meon, PhD
Professor
Faculty of Agriculture
Universiti Putra Malaysia
(Internal Examiner)

Ahmad Ismail
Professor
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Yen Peng Ting
Associate Professor
Department of chemical and bimolecular engineering
National University of Singapore
(External Examiner)

Seow Heng Fong, PhD

Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

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

Radziah Othman, PhD
Associate Professor
Faculty of Agriculture
Universiti Putra Malaysia
(Chairman)

Samsuri Abd Wahid, PhD
Lecturer
Faculty of Agriculture
Universiti Putra Malaysia
(Member)

Aminuddin Husin, PhD
Associate Professor
Faculty of Agriculture
Universiti Putra Malaysia
(Member)

BUJANG BIN KIM HUAT, PhD
Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

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 institutions.

Bahi Jalili Seh Bardan

Date: 5 January 2012

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