# Fixed Bed Biosorption of Cu(II) by Immobilized Biomass of *Sargassum baccularia*

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# *ABSTRACT*

The primary objective of this study was to investigate the feasibility of using the immobilized biomass of *Sargassum baccularia*, a brown marine macro algae, to remove and recover copper ions in a fixed bed reactor by passive adsorption. This is commonly referred to as *biosorption*. Inactivated biomass of *S. baccularia* were chemically modified by immobilizing it onto polyvinyl alcohol (PVA) as a support matrix. Spherical gel beads that were produced in this manner were subjected to mass transfer and equilibrium studies. The biosorption of copper is a bi-phasic process, with an initial fast phase for the first 2 hours followed by a slower second phase. Equilibrium was achieved after 20 hours of exposure. However, there was negligible uptake of copper by pure PVA beads. The effect of pH on biosorption equilibria was also investigated. Results indicate that copper uptake is pH dependent with higher uptake of copper at pH 6. Maximum binding capacity $q_{max}$, evaluated with Langmuir adsorption isotherm was 31.15 mg/g and 40.31 mg/g at pH 3 and pH 6 respectively. Both Langmuir and Freundlich adsorption isotherms characterized the experimental data well but Freundlich model exhibited a better fit at pH 6 than Langmuir does. To predict the adsorption profile of the immobilized biomass in a laboratory scale fixed bed reactor, a two parameter model was employed to characterize the breakthrough curve. The model was tested in various operating conditions and was able to model the entire breakthrough curve. Agreement between experimental and predicted values was favourable although minor deviations occurred at certain intervals. Reusability of the biosorbent in a fixed bed under multiple cycles of adsorption/desorption was also carried out. A bed depth of 13 cm with 1 mL/min and 20 mg/L of feed concentration was chosen. A total of three continuous cycles were studied using ethylenediaminetetraacetic acid (EDTA) at various strengths as the desorbing agent. An

elution efficiency greater than 90% indicated that copper ions were passively adsorbed onto the biomass surface and thus was easily extractable by EDTA. However, repeated exposure of the biosorbents to EDTA at 2, 4 and 6 mM reduced copper uptake in subsequent cycles. In this study, EDTA at 4 mM was found to be the optimum concentration to extract bound copper ions. At 6 mM, considerable damage was observed with copper uptake dramatically reduced. Scanning Electron Microscope (SEM) incorporating Energy Dispersive Analysis of X-ray (EDAX) was also conducted to assess the immobilized biomass surface. Both *macropores* and *micropores* were clearly observed with SEM, indicating a very porous structure for the biomass immobilized with PVA. Ion exchange took place between copper ions and two divalent ions. From the EDAX spectrum, the two divalent ions were recognized as magnesium and calcium. Both are important constituents for cell wall and metabolic activities in the algae.

# *ABSTRAK*

Objektif utama penyelidikan ini adalah untuk mengkaji kebolehan biojisim imobilis *Sargassum baccularia*, sejenis makroalga marin perang untuk menyingkir dan memulihkan ion kuprum dalam reaktor turus lapisan tetap dengan penjerapan pasif. Ia juga dikenali sebagai biopenjerapan. Biojisim inaktif (mati) *S. baccularia* diimobilasikan dengan polivinil alkohol secara modifikasi kimia. Manik-manik sfera yang terhasil darapada kaedah ini digunakan dalam aspek keseimbangan dan pemindahan jisim. Biopenjerapan ion kuprum merupakan suatu proses dwi-peringkat, dengan fasa pertama yang cepat selama 2 jam diikuti fasa kedua yang lama. Keseimbangan tercapai setelah 20 jam. Bagaimanapun, biopenjerapan oleh manik-manik asli PVA boleh diabaikan. Kesan pH keatas keseimbangan biopenjerapan juga dikaji. Keputusan menunjukkan bahawa proses biopenjerapan bergantung kepada pH dengan biopenjerapan ion kuprum yang tinggi pada pH 6. Penjerapan maksimum kuprum $q_{max}$, didapati dengan menggunakkan penjerapan isoterma Langmuir adalah 31.15 mg/g dan 40.31 mg/g pada pH 3 dan pH 6. Kedua-dua penjerapan isoterma Langmuir dan Freundlich boleh mencirikan data eksperimen biopenjerapan dengan baik tetapi model Freundlich lebih baik daripada model Langmuir pada pH 6. Untuk meramal profil penjerapan biojisim imobilis dalam reaktor turus lapisan tetap berskala makmal, model dua parameter diguna untuk mencirikan lengkung 'breakthrough'. Model ini diuji dalam berlainan keadaaan operasi dan didapati berkebolehan mencirikan kesemua lengkung 'breakthrough'. Persetujuan diantara nilai-nilai eksperimen dan ramalan adalah memuaskan walaupun terdapat sedikit peryimpangan dalam julat tertentu. Kebolehgunaan biopenjerap dalam turus lapisan tetap dengan pengitaran berbilang penjerapan/penyahjerapan juga diselidiki. Turus lapisan tetap pada ketinggian 13 cm bersama 1 mL/min dan 20 mg/L suapan dipilih sebagai keadaan operasi.

Sebanyak tiga kitaran tanpa henti dikaji menggunakan asid etilena diaminetetraasetik (EDTA) pada pelbagai kepekatan sebagai agen penyahjerap. Efisiensi nyahjerapan melebihi 90% menunjukkan bahawa ion-ion kuprum terjerap secara pasif pada permukaan biojisim, menyebabkan ia senang diekstrak oleh EDTA. Walaubagaimanapun, pendedahan berterusan biopenjerap terhadap EDTA pada 2,4 dan 6 mM menyebabkan penurunan penjerapan ion kuprum pada kitaran yang selanjutnya. Dalam kajian ini, EDTA pada 4 mM merupakan kepekatan optimum untuk mengekstrak ion-ion kuprum yang terikat. Pada kepekatan 6 mM, kerosakkan yang teruk didapati dengan penurunan penjerapan ion kuprum yang mendadak. Permukaan biojisim imobilis juga dikaji dengan mikroskop elektron (SEM) dan EDAX. Kedua-dua liang makro dan mikro jelas kelihatan dengan SEM, menunjukkan bahawa biojisim yang diimobilisikan dengan PVA merupakan struktur yang berliang. Penukaran ion juga berlaku diantara ion kuprum dengan ion-ion dwivalen. Daripada spektrum EDAX, ion-ion dwivalen ini adalah magnesium dan kalsium. Kedua-dua ion ini penting untuk perkembangan dinding sel and aktiviti metabolisme didalam alga.

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# *NOTATIONS*

| | | | |
|---|---|---|---|
| $a$ | = | surface area per volume | $m^2/m^3$ |
| $a_e$ | = | adsorption efficiency | % |
| $C_e$ | = | effluent concentration | mg/L |
| $C_{eq}$ | = | liquid phase equilibrium metal concentration | mg/L |
| $C_f$ | = | final or equilibrium metal concentration | mg/L |
| $C_i$ | = | initial metal concentration/influent concentration | mg/L |
| $C_o$ | = | initial metal concentration | mg/L |
| $C_t$ | = | metal concentration with respect to time | mg/L |
| $d_e$ | = | desorption efficiency | % |
| E | = | dispersion coefficient | $m^2/h$ |
| EDAX | = | Energy Dispersive Analysis of X-ray | - |
| erf(x) | = | error function of x | - |
| F | = | sum of the squares for experimental and model deviations | $mg^2/L^2$ |
| K | = | Freundlich constant | - |
| k | = | Langmuir equilibrium constant | L/mg |
| *k* | = | mass transfer coefficient | m/h |
| $k_1$ | = | two parameter constant | mL |
| $k_2$ | = | two parameter constant | m.h/mL |
| L | = | column length | m |
| LUB | = | length of unused bed | m |
| *l* | = | column length | m |
| M | = | amount of biomass | g |
| n | = | Freundlich exponential number | - |
| ρ | = | mass of biomass per unit volume | $g/cm^3$ |
| Q | = | column flow rate | mL/min |
| $Q_t$ | = | total adsorption efficiency | % |
| q | = | adsorbed solute concentration | mg/g |
| $q_{eq}$ | = | solid phase equilibrium metal concentration | mg/g |
| $q_{max}$ | = | Langmuir maximum adsorption capacity | mg/g |
| r | = | adsorption rate per bed volume | $mg/m^3.h$ |
| $R^2$ | = | correlation coefficient | - |
| SEM | = | Scanning Electron Microscope | - |
| t | = | time | h |
| $t_b$ | = | breakthough time | h |
| $t_0$ | = | time when $C_e = 0.5C_i$ in a fixed bed column | h |
| t* | = | time when $C_e = 0.5C_i$ in a fixed bed column | h |
| V | = | volume of metal bearing solution | L |
| z | = | axial distance | m |
| σ | = | standard deviation | - |
| $\varepsilon_b$ | = | void fraction in fixed bed | - |
| $\varepsilon_p$ | = | porosity of biosorbent | - |
| ν | = | superficial velocity | $m^3/m^2.h$ |