



**REMOVAL OF COPPER BY MARINE
ALGAL BIOMASS IMMOBILISED IN
POLYVINYL ALCOHOL BEADS**



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ABSTRACT

The main objective of this study was to investigate the feasibility of using the immobilised biomass of *Sargassum baccularia*, a brown macroalga, to remove and recover copper from aqueous solution. The technology is commonly known as biosorption. The nonliving biomass of *S. baccularia* was immobilised onto polyvinyl alcohol matrix to produce spherical gel beads. The kinetics as well as equilibrium aspects of the biosorption process were characterised. The biosorption of copper by the native biomass was a rapid process, reaching equilibrium within one hour of contact. The immobilised biomass, however, required a much longer time, about 20 hours, to attain equilibrium. The effect of solution pH on biosorption equilibria was investigated. Results indicated that copper uptake by the native as well as immobilised biomass increased with increasing pH. The maximum binding capacities of the native and immobilised biomass for copper at pH 6.0 were 1.66 and 0.63 mmol/g, respectively. Aqueous solution of ethylenediaminetetraacetic acid (EDTA) at 2 mM and hydrochloric acid (HCl) at pH 1.0 were effective desorbents. Both desorbents were able to desorb more than 90 % of the bound copper from the immobilised biomass in a single cycle of adsorption-desorption. Highly concentrated copper solution was obtained with a solid-to-liquid ratio (S/L) of 11 when HCl at pH 1.0 was used as the desorbent. The reusability of the immobilised biomass in batch systems was investigated in five consecutive cycles of adsorption-

desorption. The immobilised biomass was able to retain more than 50 % of its initial copper uptake capacity at the completion of the five cycles. The quantity of copper desorbed over the five cycles with either HCl or EDTA as the desorbent corresponded well to the quantity loaded, indicating that complete desorption was readily achieved. Continuous flow experiments were conducted by using the immobilised biomass beads in a fixed-bed column. Results showed that there was little change in column performance after three consecutive cycles of copper loading-desorption. Desorption studies showed that concentrated copper solution was obtained when the fixed-bed column was regenerated using EDTA as the desorbent. Relatively low copper concentration in the influent and low column flow rate gave satisfactory copper uptake efficiency in the fixed-bed column experiments. A simple two parameter fixed-bed model was capable of predicting the behaviour of the fixed-bed column. Although exact quantitative agreement between theoretical predictions and experimental data was not obtained, the simple model managed to predict the general behaviour of the fixed-bed column under various operating conditions.

ABSTRAK

Objektif utama penyelidikan ini adalah untuk mengkaji kebolehan imobilis biojisim *Sargassum baccularia* (sejenis makroalga perang) untuk menyingkir dan memulih ion kuprum dari larutan akuas. Teknologi ini umumnya dikenali sebagai biopenjerapan. Biojisim mati ini telah berjaya diimobiliskan dalam matriks polivinil alkohol untuk menghasilkan manik-manik berbentuk sfera. Ciri-ciri kinetik dan aspek keseimbangan proses biopenjerapan telah dikaji. Proses penjerapan ion kuprum ke atas zarah asli *S. baccularia* merupakan suatu proses yang cepat dan mencapai keseimbangan dalam masa satu jam. Akan tetapi, biojisim yang diimobiliskan memerlukan masa yang agak panjang, lebih kurang 20 jam, untuk mencapai keseimbangan. Kesan pH larutan terhadap keseimbangan biopenjerapan telah dijalankan. Keputusan eksperimen menunjukkan penjerapan kuprum oleh biojisim asli dan biojisim yang diimobiliskan bertambah apabila pH larutan bertambah. Penjerapan maksimum kuprum oleh biojisim asli dan biojisim yang diimobiliskan pada pH 6.0 didapati mencapai nilai 1.66 mmol/g dan 0.63 mmol/g masing-masing. Larutan akuas asid etilena diaminetetraasetik (EDTA) pada kepekatan 2 mM dan asid hidroklorik (HCl) pada pH 1.0 merupakan agen penyahjerapan yang berkesan. Kedua-duanya berkeupayaan menyahjerap lebih daripada 90 % kuprum yang terjerap pada biojisim yang diimobiliskan dalam satu kitaran penjerapan-penyahjerapan. Larutan berkepekatan tinggi diperolehi apabila HCl pada pH 1.0 dengan nisbah pepejal-cecair (S/L) setinggi 11 digunakan sebagai agen

penyahjerapan. Kebolegunaan semula biojisim juga dikaji dengan menjalankan kitaran penjerapan-penyahjerapan sebanyak lima kitaran berturut-turut. Selepas lima kitaran, biojisim yang diimobiliskan masih berupaya untuk menyerap logam kuprum dengan keberkesanan melebihi 50 % jika dibandingkan dengan penjerapan mula. Jumlah ion kuprum yang dinyahjerap dalam kelima-lima kitaran itu adalah lebih kurang sama dengan jumlah ion kuprum yang dijerap apabila HCl dan EDTA digunakan sebagai agen penyahjerapan. Ini menunjukkan bahawa penyahjerapan sempurna dapat dicapai. Eksperimen aliran berterusan dijalankan dengan mengalirkan larutan kuprum secara berterusan ke turus lapisan tetap yang telah diisikan dengan manik-manik biojisim yang diimobiliskan. Keputusan eksperimen menunjukkan bahawa turus lapisan tetap ini berjaya menyerap kuprum dalam tiga kitaran penjerapan-penyahjerapan tanpa mengalami perubahan besar dalam prestasinya. Kajian penyahjerapan menunjukkan EDTA berjaya menyahjerap ion kuprum dari manik-manik dengan menghasilkan larutan eluan berkepekatan tinggi. Reaktor turus lapisan tetap ini menunjukkan kecekapan penjerapan yang memuaskan apabila kepekatan aliran masuk dan kadar aliran yang lebih rendah digunakan. Satu model mudah matematik yang dikenali sebagai model dua parameter lapisan tetap berkeupayaan menjangka kelakuan turus lapisan tetap yang digunakan. Walaupun persetujuan secara kuantitatif di antara jangkauan teori dan keputusan eksperimen tidak dapat diperolehi, model mudah ini berjaya menjangka kelakuan umum turus lapisan tetap ini di bawah keadaan operasi yang berlainan.

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NOTATIONS

a	surface area per volume, m^2/m^3
C_{eq}	liquid phase equilibrium metal concentration, mM
C_f	final or equilibrium metal concentration, mM
C_i	known initial metal concentration, mM
c	solute concentration in the effluent, mM
c^*	equilibrium concentration at column outlet, mM
c_i	influent metal concentration, mM
E	dispersion coefficient, m^2/hr
$erf(x)$	error function of x
k	Langmuir equilibrium constant, mM^{-1}
k	mass transfer coefficient, m/hr
k_1	constant, mL^{-1}
k_2	constant, $hr.m/mL$
L	column length, m
M	amount of the biomass, g
Q	column flow rate, mL/min
q	adsorbed solute concentration, $mmol/g$
q_{eq}	solid phase equilibrium metal concentration, $mmol/g$ biomass
q_{max}	maximum metal adsorption capacity, $mmol/g$ biomass
r	adsorption rate per bed volume, $mmol/m^3.hr$
t	time, h
t_0	characteristic time, h
V	volume of metal-bearing solution, L
z	position, m
σ	standard deviation, dimensionless
ϵ	void fraction in the fixed-bed, dimensionless
v	superficial velocity, $m^3/m^2.hr$