BIOREMEDIATION OF METALLIC FISSION PRODUCTS IN NUCLEAR WASTE: BIOSORPTION AND BIORECOVERY

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A thesis submitted in fulfilment of requirements for the degree of

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ABSTRACT

BIOREMEDIATION OF METALLIC FISSION PRODUCTS IN NUCLEAR WASTE: BIOSORPTION AND BIORECOVERY

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The performance of a growing sulphate reducing bacteria consortium for Sr$^{2+}$, Co$^{2+}$ and Cs$^+$ removal from solution in a batch sulphidogenic bioreactor was investigated. Metal removal by the growing bacterial consortium, and microbial culture growth and metabolic activities (biological sulphate removal) were continuously monitored in the bioreactors over the duration of the treatment period. On the other hand, diversity changes within the bacterial consortium before and after bioreactor operation (28 days) were performed using the partial 16S rRNA fingerprinting method.

In the original bacterial consortium, Enterococcus and Staphylococcus sp. were the dominant bacterial species. However, the presence of Sr$^{2+}$, Co$^{2+}$ and Cs$^+$ in the growth media, resulted in the emergence of new bacterial species belonging to the Citrobacter, Paenibacillus, and Enterococcus and Stenotrophomonas genera, respectively. The Citrobacter and Paenibacillus sp. demonstrated high tolerance towards the presence of the divalent cations, Sr$^{2+}$ and Co$^{2+}$, respectively, while the Enterococcus and Stenotrophomonas sp., demonstrated Cs$^+$ high tolerance. The bacterial growth and sulphate removal rate were significantly decreased at initial metal ion concentrations $\geq$100 mg/L. The toxicity and inhibitory effects of the metals on the present SRB consortium was observed in the order Sr>Co>Cs.
The metal uptake capacity \((q_t)\) of the bacterial consortium decreased with increasing initial metal concentration, and complete Sr\(^{2+}\), Co\(^{2+}\) and Cs\(^{+}\) removal was observed at initial metal concentrations \(\leq 75\) mg/L. Overall, the present SRB consortium demonstrated a superior Sr\(^{2+}\) removal capacity \((q_{max} = 405\) mg/g\), and the least for Cs\(^{+}\), where \(q_{max} = 192\) mg/g. The present SRB culture exhibited a superior Sr\(^{2+}\) and Cs\(^{+}\) binding capacity, compared to other studies in literature. Results from Sr\(^{2+}\), Co\(^{2+}\) and Cs\(^{+}\) biosorption kinetics indicate that initial concentration and solution pH played a vital role in determining the rate of metal removal kinetics. The experimental data was successfully analysed by the pseudo-second-order rate model, demonstrating that chemisorption is the main rate limiting step for the removal of Sr\(^{2+}\), Co\(^{2+}\) and Cs\(^{+}\) from solution. In this study, the adsorption behaviour of protons and of Sr\(^{2+}\), Co\(^{2+}\) and Cs\(^{+}\) onto the bacterial consortium cell surfaces was evaluated under anaerobic conditions as a function of pH (4-10), ionic strength (0.01, 0.05, 0.1M) and temperature (25, 50 and 75°C). Acid-base titrations of the bacterial suspension indicated that the titration data could be adequately described by a four site nonelectrostatic model, with \(pK_a\) values of 4.41, 6.69, 8.10 and 10.

The Sr\(^{2+}\), Co\(^{2+}\) and Cs\(^{+}\) adsorption data could be fitted with a two site nonelectrostatic model, involving the type 1 and 2 sites (carboxylic and phosphoryl sites). Increasing the ionic strength had a negative effect on the adsorption of metal ions from solution. There was no observed temperature dependence on the adsorption of Co\(^{2+}\) and Cs\(^{+}\) from solution. In summary, results obtained in this study have shown that the processes involved in microbial Sr\(^{2+}\), Co\(^{2+}\) and Cs\(^{+}\) removal from contaminated sources is a direct function of the microbial characteristics and efficiency, mass transfer and surface complexation effects under varying environmental conditions. One important goal to be achieved in future studies will be the determination of the intrinsic stability constants and the structure of the formed metal-complexes species. These constants can be used directly in risk assessment programs.
I Nonhlanhla Ngwenya, declare that the thesis which I hereby submit for a Doctor of Philosophy in Chemical Technology degree at the University of Pretoria is my own work and has not been previously submitted by me for any degree at this or other institutions.

_________________________  ________________________
Nonhlanhla Ngwenya  Date
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‘I Owe You All More Than Words Can Tell’
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NOMENCLATURE

\( A \)  \quad \text{External sorption area (m}^2/\text{g})

\( a_{RP} \)  \quad \text{Redlich–Peterson adsorption constant ((l mg}^{-1})^2\text{)}

\( \beta \)  \quad \text{Redlich–Peterson adsorption constant}

\( b \)  \quad \text{Langmuir adsorption constant (l mg}^{-1}\text{)}

\( C \)  \quad \text{Metal concentration at time } t \text{ (mg/L)}.

\( C_{eq} \)  \quad \text{Residual metal ion concentration at equilibrium (mg l}^{-1}\text{)}

\( C_{ini} \)  \quad \text{Initial concentration of metal in solution (mg/L)},

\( C_t \)  \quad \text{Metal concentration at time } t \text{ (mg/L)}

\( C_0 \)  \quad \text{Initial metal ion concentration (mg l}^{-1}\text{)}

\( k_1 \)  \quad \text{First-order adsorption rate constant (min}^{-1}\text{)}

\( k_2 \)  \quad \text{Second-order adsorption rate constant (g mg}^{-1}\text{min}^{-1}\text{)}

\( k_C \)  \quad \text{Second-order rate coefficient (L/mg/h)}

\( k_f \)  \quad \text{External diffusion coefficient (cm/s)}.

\( k_i \)  \quad \text{Intraparticle diffusion rate (mg.g.min}^{0.5}\text{)}.

\( k \)  \quad \text{Freundlich adsorption constant}

\( K_s \)  \quad \text{Half saturation constant (mg/L)}

\( n \)  \quad \text{Freundlich adsorption constant}

\( n_p \)  \quad \text{Number of data points}

\( n_{II} \)  \quad \text{Number of chemical components for which both total and free concentration are known}

\( n_u \)  \quad \text{Number of adjustable parameters}.

\( q \)  \quad \text{Adsorbed metal ion quantity per gram of biomass at any time (mg g}^{-1}\text{)}

\( q_{eq} \)  \quad \text{Adsorbed metal ion quantity per gram of alga at equilibrium (mg g}^{-1}\text{)}
\( Q^0 \)  Langmuir adsorption constant \((\text{mg g}^{-1})\)

\( q_{\text{max}} \)  Maximum sorption capacity \((\text{mg g}^{-1})\)

\( R \)  Gas constant \((=8.314 \text{ J mol}^{-1} \text{ K}^{-1})\)

\( R^2 \)  Correlation coefficient

\( S \)  Sulphate concentration \((\text{mg/L})\)

\( S_{\text{mod}} \)  Calculated (model) concentration at time \( t \) \((\text{mg/L})\),

\( S_{\text{exp}} \)  Experimental concentration at time \( t \) \((\text{mg/L})\)

\( S_Y \)  Default experimental error calculated by FITMOD

\( t \)  Time \((\text{minutes})\)

\( T \)  Solution temperature \((\text{°C, K})\)

\( \mu \)  Specific growth rate \((1/\text{h})\)

\( \mu_{\text{max}} \)  Maximum specific growth rate \((1/\text{h})\)

\( Y \)  Error in the mass balance calculations

\( X \)  Bacterial concentration \((\text{mg l}^{-1})\)

\( Y_{x/s} \)  Bacterial yield coefficient \((\text{mg of biomass produced per mg substrate utilized})\)