BIOSORPTION OF HEAVY METALS FROM URANIUM MILL TAILINGS EFFLUENT

by

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Abstract. The present study has investigated the applicability of alginate-based biosorbents in the remediation of uranium mill tailings (UMT) effluent. For this purpose, comparative biosorption studies have been carried out with synthetic metal solutions and effluents taken from the UMT site in Durango, CO. A kinetic model has been developed to describe the rate of metal uptake (V) as a function of biosorbent concentration (B), V = V_m[B]/(K + [B]). The kinetic values, V_m and K, were derived for Cd^{2+}, Ba^{2+}, UO_2^{2+}, and Zn^{2+} sorption by calcium alginate beads. From the effect of temperature, the activation energy (∆E_a) and frequency factor (A) have been calculated to be 2.7 kcal (11.5 kJ) and 322.4 mg/l/min, respectively, for barium uptake on calcium alginate beads. Metal extractions greater than 97% were achieved. The importance of these findings relative to bioremediation of UMT is discussed.

Additional Key Words: alginate, biosorption, bioremediation, uranium mill tailings effluent.

Introduction

The introduction of biotechnological principles in the recovery of dissolved heavy metal and radionuclide contaminants from diverse industrial effluents has been gaining importance in recent years. This tendency is motivated by the fact that biosorbents (Volesky, 1986) are able to accumulate trace amounts of metal concentrations from large volumes of dilute solutions not only nonspecifically but also selectively. Therefore, biosorbents are considered for polishing effluents (Jeffers et al., 1989) which were treated first by conventional techniques such as chemical precipitation (using lime), solid and liquid ion-exchange, and reverse osmosis (Smith and Kalin, 1989).

Algae were found to remove uranium, molybdenum, and selenium ions from industrial effluents (Tsezos, 1987). The outline of the process can be given schematically as shown in Figure 1.

![Figure 1. Schematic presentation of a chemical-biological method for the treatment of uranium mine drainage.](https://doi.org/10.21000/JASMR91010141)
The process is claimed to be applicable to many mining operations where the mine needs to be dewatered. For example, water is pumped from the mine to the surface to prevent flooding. Then the drainage water is introduced into settling ponds, where the suspended colloidal particles are deposited. The clear water is lead through solid ion exchange units where the major portion of uranium and heavy metals are removed. However, if the remaining trace metal concentration is too high in the effluent water, then further purification is needed before it can be released to the environment. This can be achieved by passing the water through algal ponds (Tsezos, 1987) as shown in Figure 1. The predominant algae found in pond (A) was Spirogyra. The (B) and (C) algal ponds contained, in addition to Spirogyra, an abundant growth of Chara, especially at the bottom of the ponds. Oscillatoria and other green algae species were also observed. In the settling ponds, the presence of sulfate-reducing bacteria was detected which contributed to the formation of metal sulfide precipitation. The reduction of uranium, molybdenum, and selenium concentrations can be demonstrated by the following comparison: mine water contained 5.8 ppm U, 2.3 ppm Mo, and 0.3 ppm Se, whereas the concentrations in effluent water at the discharge of pond (C) were 0.8 ppm U, 0.8 ppm Mo, and 0.01 ppm Se.

The ability of certain fungal, yeast, algal and actinomycete species in the adsorption of uranium has been investigated (Tsezos et al., 1989). On the basis of experimental results, a flowsheet has been developed for continuous operation for biomass loading and elution. The main features of the process are outlined in Figure 2. The authors (Tsezos et al., 1989) suggested that the method can be used in the underground leaching of low-grade uranium deposits at Denison Mines, which is located in the Elliot Lake area, Ontario, Canada. According to the authors (Tsezos et al., 1989), there is no particular problem associated with the scaling up of the process. The best sorption results were obtained with Penicillium species. However, the elution of uranium from the Penicillium cells was not fully resolved. Another biosorption process has been developed for the continuous recovery of uranium from industrial bioleach solutions (Tsezos, 1987). This process used immobilized inactive Rhizopus arrhizus biomass, which was found to be an excellent selective sorbent for uranium (Tsezos, 1984, Tsezos, 1985, Tsezos et al., 1988). The biosorbent exhibited a relatively high uranium uptake capacity of about 40 mg/g (Tsezos, 1987). The pilot plant testing (loading and stripping) of the process was operating for over 100 days without any apparent reduction of the immobilized biomass uranium uptake capacity.

Radium-226, thorium-232 and uranium-238 uptake by twenty species of marine algae were studied (Edgington et al. 1970). It was found that the uptake of these radionuclides was controlled by two mechanisms: (a) ion-exchange or coprecipitation of the ions with calcium carbonate matrix, and (b) complex formation with either the protein nitrogen or some other component of the organic fraction. Radium and possibly thorium were concentrated by both of these mechanisms, while uranium only by the first mechanism. A review article (Van Der Borght et al., 1971) reported on the efficiency of sodium alginate in the removal of radium-226 from intestine of rats. Furthermore, it indicated that the formation of calcium alginate depended on the guluronic acid content of sodium alginate. The ion exchange efficiency of calcium alginate was found to increase from barium over strontium and calcium. Accumulation of radium-226 from uranium mill tailings effluent was studied (Havlik, 1971) using four
species of green algae: Ankistrodesmus falcatus var. acicularis, Chlorella vulgaris, Coelastrum cambticum, and Chlamydomonas nidulans. It was found that radium-226 uptake was dependent on the species of algae, the concentration of radium-226 in solution, the growth rate of algae and their physiological condition, and the period of exposure. Radium-226 was adsorbed onto the gelatinous capsule and the cell wall of algae mainly during the logarithmic phase. Biosorption of radionuclides from varying aqueous solutions has been studied by a number of investigators (Tsezos and Volesky, 1981, Sakaguchi et al., 1978 and Heide et al., 1975). Others (Strandberg et al., 1981) reported on microbial accumulation of radium-226, cesium-137 and uranium by Saccharomyces cerevisiae and Pseudomonas aeruginosa. The optimum pH for biosorption of radium was found to be in the neutral or slightly alkaline range (Guiseley, 1989) for Penicillium chrysogenum. Bioaccumulation of radium-226 and other radionuclides by nanoplanctonic algal species and picoplanktonic blue-green algae was determined (Kuyucak and Volesky, 1989). The algal cultures used were the centric marine diatom Thalassiosira pseudonana (clon 3H), the chlorophyte Dunaliella tertiolecta (clon Dun), the coccolithophore Emiliania huxleyi (clon MCH No.1), the filamentous cyanophyte Oscillatoria woronichini (clon Osc N4), and the picoplanktonic cyanophyte Synechoccus sp. (clon L1602). Generally, algal uptake followed the pattern Th-228 > Pb-210 > U-238 + Ra-226.

The present study will investigate the applicability of alginate beads in the removal of metallic contamination from UMT.

Alginate

Alginate is the general term used for structural polysaccharides that are extracted from some species of brown seaweed, i.e. from Macrocystis pyrifera (Guiseley, 1989). Chemically, the alginate consist of linear polymers of 1,4-linked α-D-mannuronic acid and 1,4-linked α-L-guluronic acid (called alginic acid). Their structural features are shown in Figure 3 (Pictures a and b respectively). The structure of algin polymer can have three different types of arrangement: (a) blocks of alternating mannuronic (M) and guluronic (G) residues (...MGMGMG...), blocks of mannuronic acid (...MMMMMM...), and groups of guluronic acid (...GGGGGGG...). The way these blocks are arranged controls the properties of the algin. In addition, polysaccharide chains can adopt ordered helical and ribbon like structures (Rees and Wels, 1977).

Figure 3. Structure of alginic acids.

The alginate is defined as the alkali salt of the alginic acid (Kuyucak and Volesky, 1989). The alginites are non-toxic (McNealy and Kovacs, 1975), and are widely used in foods and in other industrial applications for thickening, gelling, stabilizing, and film-forming (Guiseley, 1989). The guluronic acid-rich algin is most suited for gelling, but all algins gel in the presence of calcium ion (Rees, 1969, Morris et al., 1973). Gels made with mannuronic acid-rich algin are more brittle. The dissociation constants of mannuronic and guluronic acids were determined to be pK = 3.38 and pK = 3.65, respectively (Haug, 1964).

Kinetics of Biosorption

The kinetic evaluation of biosorption phenomena is generally described by a variety of equations, which are variations of those originally developed for gas adsorption on solid surfaces by Freundlich and Langmuir (Gregg and Sing, 1982, Itoh et al., 1975, Selvakumar and Hsieh, 1988, Xue et al., 1988, Kuyucak and Volesky, 1989). The polysaccharide-based biosorbents are known to have a complex sorption mechanism (Gadd, 1988). Metal uptake can occur simultaneously by adsorption, absorption,
chelation, and precipitation-coupled absorption. Therefore, the above kinetic approaches have a common shortcoming, since these are based on the adsorption phenomenon only. In order to avoid the above ambiguity of the kinetic interpretation and evaluation of biosorption data, a generalized rate equation has been derived that is based on the following assumptions: (a) all sites of the surface of biosorbent are identical, and (b) the biosorption process is an equilibrium phenomenon. If the sorption of X metal ionic species occurs on one of the surface sites of biosorbent (B), then it can be expressed as:

\[
X + B = XB
\]  
(1)

where XB is the amount of metal uptake. For molar solutions, the equilibrium constant can be expressed as (Gadd, 1988, Leja, 1982):

\[
K_{eq} = [XB]/([X][B])
\]  
(2)

Let us suppose that from the original X concentration \(X_1\) is sorbed so that the free metal ion concentration in solution is \(X-X_1\). Therefore equation 2 can be rewritten as:

\[
K_{eq} = [X_1]/([X-X_1][B])
\]  
(3)

The fraction of metal adsorbed, \(\varepsilon\), is given by:

\[
\varepsilon = X_1/X
\]  
(4)

or

\[
X_1 = \varepsilon X
\]  
(5)

Substituting equation 5 into equation 3, yields

\[
K_{eq} = \varepsilon X/([X-\varepsilon X][B])
\]  
(6)

from where

\[
\varepsilon = K_{eq}[B]/(1 + K_{eq}[B])
\]  
(7)

Let \(V\) be the rate of metal uptake by the biosorbent and be proportional to the amount of metal sorbed as a function of time:

\[
V = k\varepsilon \quad \text{or} \quad \varepsilon = V/k
\]  
(8)

where \(k\) is the reaction rate constant. The substitution of \(\varepsilon\) into equation 7 will yield:

\[
V/k = K_{eq}[B]/(1 + K_{eq}[B])
\]  
(9)

However, when all metallic species are sorbed, \(\varepsilon = 1\) so that

\[
k = V_m
\]  
(10)

where \(V_m\) is the maximum theoretically obtainable rate of metal uptake. Inserting equation 10 into 9 gives:

\[
V = V_mK_{eq}[B]/(1 + K_{eq}[B])
\]

\[
= V_m[B]/(1/K_{eq} + [B])
\]

(11)

The \(1/K_{eq}\) is redefined to be equal to a constant \(K\), which is the concentration of biosorbent that results in the \(V_m/2\). Therefore, it can be written:

\[
V = V_m[B]/(K + [B])
\]

(12)

Equation 12 is similar to the Monod's empirical hyperbolic rate equation (Monod, 1949), and it has general applicability for the mathematical description of all biosorption rate phenomena. Equation 12 is used in the current study for the description of metal ion uptake phenomena.

**Materials and Methods**

**Bead Precursor Material**

Bead precursor material was prepared by adding 3.0 g dry sodium alginate powder (Keltone HV gelling grade, Kelco Co., Chicago, IL) to 97 g pure water (Barnstead, NANOpure II Water System, Boston, MA) in the mixing cup of a Waring blender and homogenizing it at a low speed setting for 5 to 6 minutes. The solution was transferred into a 250 ml beaker, autoclaved for 15 minutes at 120°C, and allowed to cool to room temperature.

**Bead Formation**

The bead precursor material was placed into a stainless steel dispenser, whose schematic outline is shown in Figure 4. The dispenser was pressurized by compressed air to force the precursor mass to leave the dispenser through the gauge holes as droplets which were collected in 500 ml of 0.1 M CaCl\(_2\) solution and was stirred for 10 minutes. Then, 2.5 g polyethyleneimine (PEI) was added and the solution stirred for 5 minutes. This was followed by the addition of 500 ml of pure water, and shortly after the beads were filtered and washed with distilled water.
Compressed air

![Schematic of dispenser used to form calcium alginate beads.]

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**Figure 4.** Schematic of dispenser used to form calcium alginate beads.

**UMT Effluents**

Uranium mill tailing effluents were taken from the UMT controlled containment site in Durango, CO. The solution samples were analyzed for their heavy metal and radionuclide contents and used in the column remediation experiments.

**Biosorption**

This series of experiments was performed in 500 ml reactors containing 400 ml synthetic solutions of varying concentrations of single metals at pH 5.0, 200 rpm, and 23°C temperature. The metal uptake by the beads was followed by periodically removing 1.0 ml samples from the experimental solutions for analysis.

**Column Studies**

This series of experiments was carried out at room temperature with 300 ml Ca-alginate beads (8.5 g dry weight of sodium alginate) and 1 liter UMT effluent. The Ca-alginate beads were introduced into a 500 ml glass column and charged with the mill tailings effluents at rates of 2 ml per minute. The throughflow was collected in 15 ml samples and analyzed for heavy metals and radionuclides. The schematic outline of the experimental setup is shown in Figure 5.

![Schematic outline of the experimental setup used for calcium alginate column studies.]

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**Analytical Methods**

Heavy metal ion concentrations of different aqueous samples were assessed by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP), (Applied Research Laboratories, Model 3520) and radionuclides by gamma ray spectroscopy (Princeton Gamma Tech and EG&G Ortec).

**Results and Discussion**

**Effects of Alginate Bead Concentration**

This series of experiments was carried out with synthetic single metal solutions containing 50 ppm barium, cadmium, uranyl or zinc concentration, and 150-200 mg/l calcium-loaded alginate beads at 23°C and 200 rpm. Figure 6 presents the zinc uptake data as a function of time. As it can be seen, the zinc uptake increases with the time of treatment and Ca-alginate bead concentration. The data points...
were fit with a first-order logarithmic equation:

\[ Y = a + b \ln(t) \]  

(13)

where \( Y \) is the zinc uptake in mg/l by the biosorbent, \( t \) is the time of treatment in minutes, and \( a \) and \( b \) are regression coefficients. The constant values \( (a \) and \( b \) and the \( R^2 \) for the overall have been calculated for each experimental run by the logarithmic regression technique and the data reported in Table 1. The fitted lines calculated with the help of equation 13 using the regression coefficients from Table 1 are also indicated in Figure 6. The relative high \( R^2 \) values in Table 1 suggest a good fit for the experimental data for zinc uptake by the biosorbent.

The initial average rate of zinc (V, mg/l/min) uptake has been defined as the mass of zinc sorbed by the biosorbent in the initial 5 minutes of treatment. Thus, the \( V \)-values have been calculated for each series with the appropriate bead concentration \( (B) \) using the regression analysis data of Table 1 in equation 13. These results are indicated in the last column in Table 1. Figure 7 is the linearized graphical presentation of equation 12, achieved by plotting the inverse of zinc uptake rate \( (1/V) \) versus the inverse of calcium-alginate bead concentration \( (1/B) \). The intercept of the regression analysis line with the \( 1/V \) axis corresponds to \( 1/V_m \) and the slope of the straight line corresponds to \( K/V_m \). From this presentation the \( V_m \) and \( K \) values have been determined to be 7.4 mg/l/min and 1839 mg/l, respectively.

Table 1. Regression analysis data of zinc uptake experiments.

<table>
<thead>
<tr>
<th>Bead Concentration ( (B, \text{mg/l}) )</th>
<th>( a )</th>
<th>( b )</th>
<th>( R^2 )</th>
<th>( V ) ( \text{(mg/l/min)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>-1.12494</td>
<td>2.59481</td>
<td>0.98438</td>
<td>0.60125</td>
</tr>
<tr>
<td>250</td>
<td>-2.95572</td>
<td>4.07779</td>
<td>0.99179</td>
<td>0.72142</td>
</tr>
<tr>
<td>500</td>
<td>-3.19952</td>
<td>6.04574</td>
<td>0.97650</td>
<td>1.50605</td>
</tr>
<tr>
<td>750</td>
<td>2.522565</td>
<td>6.24254</td>
<td>0.97521</td>
<td>2.51543</td>
</tr>
<tr>
<td>1000</td>
<td>7.26749</td>
<td>6.20714</td>
<td>0.94148</td>
<td>3.45150</td>
</tr>
</tbody>
</table>

Similarly to zinc biosorption experiments, the cadmium, barium, and uranyl ion uptakes were studied with calcium-alginate bead concentrations varying from 100 to 2000 mg/l, and this data is summarized in Table 2 in terms of \( V_m \) and \( K \) values. No data are available from the literature for comparison of the kinetic values derived in this investigation. However, the smaller \( K \)-values indicate a higher loading efficiency of the biosorbent material.
Table 2. Summary of metal uptake data by Ca-alginate biosorbent.

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>( V_m ) (mg/I/min)</th>
<th>( K ) (mg/I)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd(^{2+} )</td>
<td>17.4</td>
<td>2663</td>
</tr>
<tr>
<td>Ba(^{2+} )</td>
<td>24.7</td>
<td>4343</td>
</tr>
<tr>
<td>UO(_{2}^{2+} )</td>
<td>10.6</td>
<td>1303</td>
</tr>
<tr>
<td>Zn(^{2+} )</td>
<td>7.4</td>
<td>1839</td>
</tr>
</tbody>
</table>

**Effect of temperature**

The effect of temperature was studied for barium uptake by the calcium-alginate beads in the range of 20 to 65°C using 50 ppm Ba\(^{2+} \) (BaCl\(_2\)) solutions and 1500 mg/I bead concentration. The biosorption data were evaluated as it was shown for the zinc uptake experiments, and the rate of barium uptake related to the temperature by the Arrhenius equation (Laidler and Meiser, 1982):

\[
V = A e^{\Delta E_a/RT}
\]

(14)

where \( A \) is the frequency factor, \( \Delta E_a \) is the activation energy, and \( T \) is the temperature in degree Kelvin. Equation 14 can be linearized by taking its logarithm:

\[
\ln(V) = \ln(A) - \Delta E_a/RT
\]

(15)

A plot of \( \ln(V) \) versus \( 1/T \) yields a straight line whose intercept with the \( \ln(V) \) axis corresponding to \( \ln(A) \) and slope to \( -\Delta E_a/RT \), from which the frequency factor and activation energy can be approximated. Figure 8 shows the linearized Arrhenius plot for barium uptake by calcium-alginate beads.

This presentation is typical for the temperature effect of chemical and biochemical reactions. The \( \Delta E_a \) and \( A \) values derived for barium biosorption are 2.7 kcal (11.5 kJ) and 322.4 mg/I/min, respectively. The relatively low activation energy suggests that this biosorption process is diffusion controlled, and it involves the formation of an activated complex:

\[
\text{Ba}^{2+} + \text{B} = \{\text{BaB}\} - \text{Ba-B}
\]

where the formation of the activated complex \( \{\text{BaB}\} \) is a slow equilibrium process that transforms fast to product, barium loaded alginate Ba-B, which is the barium alginate.

**Remediation of Uranium Mill Tailing Effluent**

The biosorption column was charged with 300 ml calcium-alginate beads (corresponding to 8.5 g alginate, dry weight) and contacted with one liter of uranium mill tailing effluent in 15 ml/min flow rate. The through-flow solution was continuously sampled and analyzed. It was found that approximately 200 ml of UMT effluent could be remediated with the beads in the column when the beginning of breakthrough occurred. Partial remediation was continued until about 400 ml of UMT effluent passed through when the complete breakthrough occurred. The difference in the metal ion concentration of inflow UMT effluent and initial breakthrough solution is compared in Table 3. Accordingly, the removal of various metal ions from the UMT effluent was 54 to 87%.

The biosorption approach for the remediation of UMT sites, where the underground water is contaminated, can be done by the pump and treat method. In this process, the contaminated ground water is pumped to the surface and treated by one of the conventional methods (Smith and Kalin, 1989), after which, the remaining trace concentrations could be removed by a biosorption process as suggested in this study.

The information generated in this investigation is preliminary in nature and does not represent the final capabilities of the process. Further studies are in progress using carrageenan, dextran, dextran sulfate, and xanthan gum based calcium and/or barium loaded beads for the remediation of uranium mill tailing effluents.
### Table 3. Bioremediation of actual UMT effluent.

<table>
<thead>
<tr>
<th>Metal Ion</th>
<th>UMT effluent (ppm)</th>
<th>Remediated effluent (ppm)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>17.3</td>
<td>3.7</td>
<td>78</td>
</tr>
<tr>
<td>U</td>
<td>4.5</td>
<td>0.99</td>
<td>78</td>
</tr>
<tr>
<td>V</td>
<td>&gt;4.9</td>
<td>0.90</td>
<td>&gt;82</td>
</tr>
<tr>
<td>Mo</td>
<td>1.4</td>
<td>0.36</td>
<td>74</td>
</tr>
<tr>
<td>Mn</td>
<td>1.18</td>
<td>0.16</td>
<td>86</td>
</tr>
<tr>
<td>P</td>
<td>0.74</td>
<td>0.34</td>
<td>54</td>
</tr>
<tr>
<td>Sr</td>
<td>0.25</td>
<td>0.10</td>
<td>60</td>
</tr>
<tr>
<td>S</td>
<td>525.</td>
<td>132</td>
<td>75</td>
</tr>
<tr>
<td>Ca</td>
<td>578.</td>
<td>197</td>
<td>66</td>
</tr>
<tr>
<td>Na</td>
<td>200.</td>
<td>30.</td>
<td>85</td>
</tr>
<tr>
<td>Mg</td>
<td>76.</td>
<td>10.</td>
<td>87</td>
</tr>
</tbody>
</table>

### Summary

The biosorbent (immobilized calcium-alginate beads) reported in this study has indicated a good potential for the remediation of uranium mill tailing effluents. It was found to be especially efficient for the removal of certain actinide and heavy metal ions from UMT effluent. The kinetic studies with synthetic single metal ion solutions contribute to a better understanding of the biosorption phenomena. Further studies are in progress.

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