BIOSORPTION OF URANIUM ON SARGASSUM BIOMASS

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Abstract—Protonated, non-living biomass of the brown alga Sargassum fluitans effectively sequestered uranyl ions from aqueous solution, with the maximum uranium sorption capacity exceeding 560 mg/g, 330 mg/g and 150 mg/g at pH 4.0, 3.2 and 2.6, respectively. At various pH levels, batch sorption equilibrium was reached within 3 h and the sorption isotherms were interpreted in terms of the Langmuir model. The sorption system pH profoundly affected uranium sorption capacities and sorption mechanisms through the hydrolysis of uranyl ions in aqueous solution. While only UO$_2^{2+}$ ions existing at pH 2.6 were exchanging with protons on the biomass, the high uranium sorption at pH 4.0 was attributed to the existence of hydrolysed uranyl ions, UO$_2$OH$_2^-$, (UO$_2$)$_2$(OH)$_5^{2+}$ and (UO$_2$)$_3$(OH)$_4^{2+}$. Each mole of uranium binding to the biomass was accompanied by the consumption of approximately 2 mol of LiOH for maintenance of the desired constant pH. The uranium could be easily recovered from the metal-loaded biomass by elution with 0.1 N HCl. The desorption was complete and the damage to the biomass was slight. These findings indicate an enormous potential of biosorption in uranium removal from aqueous solutions.

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Key words—biosorption, biosorbent, equilibrium, uranium, alga, Sargassum

GLOSSARY

$C_i$, $C_f$ Initial and final metal concentration (mmol/L)

$C_{des}$ Metal concentration in the eluant solution (mmol/L)

$k$ Parameter in the Freundlich sorption isotherm relationship

$K$ Equilibrium constant in the Langmuir sorption isotherm relationship

$n$ Parameter in the Freundlich sorption isotherm relationship

$q$ Metal uptake (mmol/g)

$q_m$ Maximum (Langmuirian) metal uptake

$q_{des}$ Eluted metal content per gram of biomass

$V$ Solution volume (L)

$W$ Biomass weight (g)

INTRODUCTION

Biosorption of dangerous elements from nuclear waste liquids has attracted a significant focus in recent years (Ashley and Roach, 1990; Macaskie, 1991). Uranium is one of the most seriously threatening heavy metals because of its high toxicity and some radioactivity. Excessive amounts of uranium have found their ways into the environment through the activities associated with the nuclear industry (Benedict et al., 1981). Uranium contamination poses a threat in some surface and groundwaters (Laul, 1992; White, 1983). Various non-living biomass types such as those of filamentous fungi, yeast, bacteria, actinomycetes etc., have been reported to bind uranium in excess of 150 mg/g of dry biomass (Volesky and Tsezos, 1981; Guibal et al., 1992; Macaskie et al., 1992; Munroe et al., 1993; Hu et al., 1996). The fresh water algae such as Chlorella regularis and vulgaris, also demonstrated a good uranium adsorption performance (Horikoshi et al., 1979; Byerley et al., 1987). Although the fact that the marine algae are capable of biologically concentrating radionuclides such as radium, thorium and uranium has been known for long time (Edgington et al., 1970), the biosorption of uranium by non-living marine algae has rarely been reported. Marine algae proliferate ubiquitously and abundantly in the litoral zones of world oceans, they are rather stable and fast growing. The biosorption capacity of the non-living marine algae for various metals was summarized by Kuyucak and Volesky (1990). The brown alga Sargassum fluitans has been found particularly effective in binding heavy metal ions of gold, cadmium, copper and zinc etc. (Volesky and Holan, 1995). The high sorption capacity, easy regeneration and low-costs make
this biomass of special interest for the purification of high volumes of wastewater with lower concentration levels of metal toxicity to be removed (Kuyucak and Volesky, 1989; Aldor et al., 1995; Leusch et al., 1995; Volesky and Holan, 1995). This is either difficult and/or expensive to accomplish by conventional metal-removal processes. The present work extended the investigation of the biosorption by the Sargassum alga biomass to the uranium removal and recovery. In this work, basic parameters of uranium biosorption equilibrium were determined and the biosorption mechanisms elucidated at various pH values. Uranium desorption was also examined.

**MATERIALS AND METHODS**

**Preparation of sorbent**

Beach-dried Sargassum fluitans, collected in Naples, FL, was ground in a homogenizer and sieved to different fraction sizes. The batch of biomass with particle size 1.0–1.4 mm was selected for subsequent protonation pretreatment aimed at standardizing the biomass by eliminating the light metals Ca²⁺, Mg²⁺ etc. The protonation wash was conducted at various pH values. Uranium desorption was determined and the biosorption mechanisms elucidated.

**Metal concentration analysis**

Dissolved uranium and lithium concentrations in solution were assessed simultaneously by an inductively coupled plasma atomic emission spectrophotometer (ICP-AES, Thermo Jarrel Ash, Model TraceScan). The ICP analyses were conducted at wavelengths of 409.014 nm and 367.8 nm for uranium and lithium, respectively. Experimental samples were filtered or centrifuged before they were introduced into the ICP system. Trial tests were made to ensure that no sorption of dissolved metals occurred on the filter assembly.

**Sorption dynamics experiments**

In order to determine the contact time required for the sorption equilibrium experiments, the sorption dynamics experiments were conducted first. 0.1 gram of biomass was mixed with 50 mL of 0.1 N HCl in a 250 mL Erlenmeyer flask. The remaining procedure was the same as that in the sorption equilibrium experiments except that no pH adjustment was required. The eluted biomass metal content could be calculated directly from the amount of metals desorbed into the HCl solution as follows:

\[ q_{\text{des}} = \frac{C_{\text{des}}V}{W} \]

with \( V \) being the solution volume, and \( W \) being the mass of biosorbent.

In the desorption experiments, 0.1 g of metal-loaded biomass was mixed with 50 mL 0.1 N HCl in a 250 mL Erlenmeyer flask. The remaining procedure was the same as that in the sorption equilibrium experiments except that no pH adjustment was required. The eluted biomass metal content could be calculated directly from the amount of metals desorbed into the HCl solution as follows:

\[ q_{\text{des}} = \frac{C_{\text{des}}V}{W} \]

with \( q_{\text{des}} \) being eluted metal content per gram of biomass and \( C_{\text{des}} \) being the metal concentration in the HCl eluant solution.

**RESULTS**

**Sorption isotherms at different pH values**

In order to determine the minimum contact time for the equilibrium experiments, the sorption dynamics was examined first. The results are demonstrated in Fig. 1 where the profiles of dimensionless uranium concentration vs contact time are plotted. The uranium biosorption rate was strongly influenced by the sorption system pH value, the residual solution concentration decreased with contact time faster at higher pH values. At various pH values, approximate 70–80% of the uranium present originally in the solution was sorbed onto the biomass in about 15 min after the start of biosorption and the equilibrium could be reached within 3 h. This provided a guide for the biosorption contact time to be used in the following equilibrium experiments.

The resulting isotherms for equilibrium uranium biosorption on Sargassum biomass at pH 2.6, pH 3.2 and pH 4.0 are plotted in Fig. 2. Each of these isotherms could be reasonably represented by either Langmuir (solid lines) or Freundlich (dashed lines) sorption models. The model parameters are listed in Table 1. Langmuir model parameters are \( q_m \) (the maximum uptake capacity) and \( K \) (the equilibrium constant), whereby Freundlich model employs the frequency factor \( k \) and the exponential factor \( n \). Those parameters were obtained by non-linear re-
gression using KaleidaGraph® software. At pH 2.6 and pH 3.2, the Langmuir model regression resulted in higher correlation coefficients than those obtained for the Freundlich model fits. However, at pH 4.0, the Freundlich model could represent the isotherm better. The Langmuir model parameters were largely dependent on the final solution pH values. The maximum sorption capacity $q_m$ increased while the Langmuir equilibrium constant $K$ decreased for higher solution pH values. This indicated that the sorption affinity of uranium for the biomass was enhanced at higher solution pH values. It is also worth noting that the $q_m$ value at pH 4.0 was close to the total amount of biomass binding sites, 2.25 mmol/g, which was determined by acid–base titration of the Sargassum biomass (Schiewer et al., 1995; Fourest and Volesky, 1996).

Since there was no micro-precipitation observed in any of the control samples, the very high uranium biosorption uptake could be attributed only to biosorption by biomass involved in the metal-binding and removal process.

**Sorption stoichiometry for different pH values**

Uranium biosorption on the protonated Sargassum biomass was accompanied by the release of protons from the biomass, which would normally cause a decrease in the solution pH. In order to maintain constant pH values, LiOH solution was metered into the sorption system. It was consumed not only in neutralization of the released protons but also in the sorption of Li on the biomass. The...
The molar uranium uptake was observed to be proportional to the amount of LiOH added to the solution. The molar ratio of the uranium uptake to LiOH consumption was 1:2.06 (regressed in Fig. 3). This linear relationship was matched at various pH values.

Desorption of uranium by HCl

The uranium-loaded biomass was eluted by various elutants, NaHCO₃, (NH₄)₂SO₄ and by mineral acids. The mineral acids such as diluted H₂SO₄, HNO₃ and HCl, were effective in uranium desorption and the biomass damage caused by the acid elution was negligible. For example, the uranium-loaded biomass with various initial uranium loadings could be eluted by 0.1 N HCl solution almost completely, as seen in Fig. 4 where the amount of the desorbed uranium and the corresponding initial uranium loading was plotted against the equilibrium uranium concentration at pH 4.0. The good agreement of the two curves indicated that the desorption with 0.1 N HCl was complete. The biomass weight loss during the acidic desorption process was less than 5%. The biomass was also protonated at the same time and was ready for the next run of uranium biosorption. The high elution efficiency, low biomass damage and low-cost made the dilute mineral acid elution quite appropriate for further consideration. Cursory observations on the biomass uranium uptake performance in several subsequent biosorption cycles indicated that less than 5% deterioration per cycle can be expected. More extensive studies on the effects of the regeneration procedure effect were considered to be beyond the scope of this work.

DISCUSSION

The effect of pH on uranium biosorption mechanisms and the maximum sorption capacity has been examined. The metal ion binding in biosorption could be attributed to several mechanisms such as ion exchange, complexation, electrostatic attraction and microprecipitation. For alga biomass, ion exchange was shown to play an important role in the metal sequestering mechanism (Crist et al., 1988, 1993). The ion exchange mechanism for uranyl ions binding to the biomass was complicated by the fact that the uranium cation UO₂⁺ is hydrolyzed in an aqueous solution within the range of the sorption system pH. The repartitioning of the hydrolysed uranium species depends on the solution pH and on the total uranium concentration in the solution. In the range of acidic to near neutral pH values, four major hydrolysed complex ions, UO₂⁺, (UO₂)₂(OH)₂⁺, UO₂OH⁺, (UO₂)₃(OH)₅⁺ and dissolved solid schoepite (4UO₃·9H₂O), a hydrous uranium oxide, exist in the solution. The hydrolysis equilibria are as follows (Baes and Mesmer, 1976):

\[
\text{UO}_2^{2+} + \text{H}_2\text{O} \leftrightarrow \text{UO}_2\text{OH}^+ + \text{H}_3\text{O}^+ \quad \text{pK} = 5.8
\]

\[
2\text{UO}_2^{2+} + 2\text{H}_2\text{O} \leftrightarrow (\text{UO}_2\text{OH})_2^{2+} + 2\text{H}_3\text{O}^+ \quad \text{pK} = 5.62
\]

![Fig. 3. Comparison of the uranium sorption uptake and the LiOH consumption. (▲) pH 2.6; (●) pH 3.2; (■) pH 4.0; (———) Regressed line, slope = 2.057.](image-url)
3UO$_2$$^+$ + 5H$_2$O $\leftrightarrow$ (UO$_2$)$_3$(OH)$_5$$^+$ + 5H$_3$O$^+$

$\text{pK}_s = 15.63$

where $\text{pK}_s$s are the logarithms of the equilibrium constants. Equilibrium calculations could be carried out by a computer program MINEQL+ (Schecher, 1991).

At pH 2.6, UO$_2$$^+$ is the dominant ion form in the solution for a wide uranium concentration range from 0.3 to 1000 ppm. The UO$_2$$^+$ is capable of competing with protons for the binding sites on the biomass in an ion exchange manner. Since the UO$_2$$^+$ is divalent, it can only replace two protons on the adjacent binding sites of the biomass but cannot react with those sites which are farther apart from each other. In other words, at low pH some binding sites are not available to the divalent UO$_2$$^+$. The approximate stoichiometric relationship of approximately 1:2 for UO$_2$$^+/\text{OH}^-$, obtained in Fig. 3, reflected the divalent-to-monovalent ion exchange characteristics. In Fig. 2 and Table 1, the experimental maximum uranium uptake capacity was 0.7 mmol/g which accounted for 62% of the total binding sites or initial proton capacity of biomass (2.25 meq/g).

At pH 4.0, all monovalent and divalent hydrolyzed ions UO$_2$OH$^+$, (UO$_2$)$_2$(OH)$_3$$^+$ and (UO$_2$)$_3$(OH)$_5$$^+$ existed in the solution in all experimental concentration ranges of uranium. The ionic composition of the uranium solution at pH 4.0 was as in Fig. 5 (Schecher, 1991). The percentage of UO$_2$$^+$ decreased while that of (UO$_2$)$_2$(OH)$_3$$^+$ increased with the increase in the total uranium concentration. The two monovalent ions took about 10–15% of the total in all concentration ranges. According to Collins and Stotzky (1992), the hydrolyzed species can apparently be sorbed better than the free hydrated ions. Particularly, compared with the divalent hydrolyzed ions, the monovalent ions have even higher affinity to the biomass in ion exchange with protons because they could replace single protons on separate binding sites in the biomass. The binding of the hydrolyzed ions onto the biomass would drive the hydrolysis equilibrium toward formation of hydrolyzed complex ions when the accumulation of the H$_3$O$^+$ was neutralized by adding the LiOH to the system in order to maintain the constant solution pH 4.0. Eventually, the uranium would be sorbed on the binding sites in the form of hydrolyzed ions. When the hydrolyzed ions exchanged with protons, the ion exchange stoichiometry was as follows:

UO$_2$OH$^+$ + H$^+$ $\leftrightarrow$ UO$_2$OH$^+$$^-$ + B + H$^+$ \hspace{1cm} (6)

(UO$_2$)$_2$(OH)$_3$$^+$ + H$^+$ $\leftrightarrow$ (UO$_2$)$_2$(OH)$_2$$^+$ - B + H$^+$ \hspace{1cm} (7)

(UO$_2$)$_3$(OH)$_5$$^+$ + 2H$^+$ $\leftrightarrow$ (UO$_2$)$_3$(OH)$_4$$^+$ - B$_2$ + 2H$^+$ \hspace{1cm} (8)

From equation (6), the reaction stoichiometric ratio would be 1:1 for U/H$^+$, 3:1 for U/H$^+$ from equation (7), and 2:2 for U/H$^+$ from equation (8), instead of 1:2 for U/H$^+$ in the case of UO$_2$$^+/\text{H}^+$ exchange. The maximum molar uranium uptake could thus become higher than the value for the total binding capacity in the biomass, i.e. 2.25 meq/g. The actual experimental $q_m$ value of 2.4 mmol/g at pH 4.0 Table 1 agreed with the expected value.

Combining equations (3) and (6), equations (4) and (7), equations (5) and (8), respectively, it could be observed that one mole of UO$_2$$^+$ sorption in the
form of hydrolyzed ions produced 2 mol of protons in all cases. Thus, in order to maintain the constant solution pH at 4.0, two moles of LiOH would be required to neutralize the released protons for every one mole of uranium sequestered. This was well supported by the result obtained in stoichiometry experiments (Fig. 3).

At pH 3.2, the interaction of the UO$_2^{2+}$ hydrolysis and ion exchange within this intermediate pH range was between the above two cases. The monovalent hydrolyzed ions UO$_2$OH$^+$ started to appear in the solution even when the uranium concentration was very low, for example, UO$_2$OH$^+$ represented 1.3% of the total 0.3 ppm uranium in solution at pH 3.2. The existence of the hydrolyzed ions, particularly the monovalent ones, enhanced the ion exchange during the sorption process. The experimental $q_m$ value of 1.4 mmol/g at pH 3.2 Table 1, or 2.8 meq/g for UO$_2^{2+}$, was about 25% higher than what would correspond to the amount of total binding sites (2.25 meq/g). The excessive uptake reflected the sorption of hydrolyzed ions. Just as the case was at pH 4.0, the 1: 2 of U/OH$^-$ ratio was maintained for the same reason.

At higher pH values, the non-ion dissolved solid schoepite started appearing in the solution. The decrease in ion concentration hindered the uranium sorption. Guibal et al. (1992) observed a decrease in uranium uptake on filamentous fungus biomass at pH 6.0.

In summary, the biosorption of uranium on Sargassum biomass is a ion exchange process between the uranium ions and protons introduced to the biomass binding sites during the acid pre-treatment. The hydrolysis of uranium ions, which is dependent on the solution pH, increased the uranium uptake by forming monovalent hydrolyzed complex ions. The number of available binding sites in the biomass for hydrolyzed ions was twice or more than that for the divalent free UO$_2^{2+}$ ions. Correspondingly, at pH 4.0, the maximum uranium uptake was as high as 566 mg/g or 2.38 mmol/g, which is somewhat higher than would theoretically correspond to the total biomass binding sites.

### REFERENCES


