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**CRADA Final Report
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**DEVELOPMENT AND
DEMONSTRATION OF
BIOSORBENTS FOR CLEAN-UP OF
URANIUM IN WATER**

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DEVELOPMENT AND DEMONSTRATION OF BIOSORBENTS FOR CLEAN-UP OF URANIUM IN WATER

Final CRADA Report ORNL 91-0075

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and
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ABSTRACT

Pseudomonas aeruginosa strain CSU, a nongenetically engineered bacterial strain known to bind dissolved hexavalent uranium (as UO_2^{2+} and/or its cationic hydroxo complexes), was characterized with respect to its sorptive active (equilibrium and dynamics). Living, heat-killed, permeabilized, and unreconstituted lyophilized cells were all capable of binding uranium. The uranium biosorption equilibrium could be described by the Langmuir isotherm. The rate of uranium adsorption increased following permeabilization of the outer and/or cytoplasmic membrane by organic solvents such as acetone. *P. aeruginosa* CSU biomass was significantly more sorptive toward uranium than certain novel, patented biosorbents derived from algal or fungal biomass sources. *P. aeruginosa* CSU biomass was also competitive with commercial cation-exchange resins, particularly in the presence of dissolved transition metals. Uranium binding by *P. aeruginosa* was clearly pH dependent. Uranium loading capacity increased with increasing pH under acidic conditions, presumably as a function of uranium speciation and due to the H^+ competition at some binding sites. Nevertheless, preliminary evidence suggests that this microorganism is also capable of binding anionic hexavalent uranium complexes. Ferric iron was a strong inhibitor of uranium binding to *P. aeruginosa* CSU biomass, and the presence of uranium also decreased the Fe^{3+} loading when the biomass was not saturated with Fe^{3+} , suggesting that Fe^{3+} and uranium may share the same binding sites on biomass. Although the equilibrium loading capacity of uranium was greater than that of Fe^{3+} , this biomass showed preferences of binding Fe^{3+} over uranium. Thus a two-stage process in which iron and uranium are removed in consecutive steps was proposed for efficient use of the biomass as a biosorbent in uranium removal from mine wastewater, especially acidic leachates.

P. aeruginosa CSU shows particular promise as the basis of an immobilized-cell process for removal of dissolved uranium from contaminated wastewaters. A number of polymeric materials, including calcium alginate, polyacrylamide, polysulfone, and polyurethane, were evaluated as possible immobilization matrices for lyophilized biomass of *P. aeruginosa* CSU. Polyurethane-based materials such as hydrogel were identified as superior candidates for biomass immobilization. A novel polyurethane gel-bead fabrication technique was developed and successfully demonstrated at pilot-plant scale for producing mass quantities of spherical, uniform-size beads. The immobilized bacterial biomass was evaluated via the measurement of sorption isotherms and dynamics within a batch, stirred-tank reactor; and loading and elution behavior within a continuous, upflow, packed-bed columnar reactor. Sorption equilibrium and dynamics in a batch stirred tank were modeled with a pore-diffusion mass transfer model, by which a pore-diffusion coefficient was determined to be approximately $2.0 \times 10^{-6} \text{ cm}^2/\text{s}$ for uranyl ion transport through the polyurethane gel matrix. The biosorbent beads were regenerable with dilute (0.01–0.1 M) sodium carbonate solutions. Preliminary column breakthrough-elution studies indicated that *P. aeruginosa* CSU biomass immobilized within polyurethane gel beads was effective for removal of uranium from low-concentration, acidic wastewaters.

STATEMENT OF THE OBJECTIVES

The goal of this collaborative research and development agreement (CRADA) and the corresponding R&D project was the discovery, development, and demonstration of a novel biological process for the removal of dissolved uranium, present in low concentrations (~10 ppm, or 10 mg/L) in acidic (~pH 2.5) wastewaters obtained from uranium mining and milling activities. This process would consist of a chromatography column containing microbial biomass as a uranium sorbent; the column would be operated semicontinuously, in an upflow mode, permitting a decrease in dissolved uranium levels to meet proposed World Health Organization standards (≤ 1 mg/L). The process was designed to be integrated into typical unit operations (e.g. precipitation) at the remediation site. The biosorbent was also to be reusable over several sorption/desorption cycles via the use of nonhazardous stripping agents. Bound uranium was to be immobilized onto or within the biomass, preventing spontaneous release.

BENEFITS TO THE FUNDING DOE OFFICE'S MISSION

The project was successful in that it further characterized a previously-identified microbial sorbent; some of the new findings are provided in the attached paper, "Biosorption of uranium by *Pseudomonas aeruginosa*...: characterization and comparison studies." Further preliminary work within this project showed that bound hexavalent uranium was actually precipitated intracellularly in its tetravalent form, presumably as insoluble uraninite. [A paper detailing this finding is in preparation.] A novel polyurethane gel immobilization matrix was developed during this project, as described in "Biosorption..immobilized in a novel matrix" (attached). The product of this work is a new sorbent plus matrix which together are efficient, inexpensive, rapid, and nonhazardous (**better/cheaper/faster/safer**).

TECHNICAL DISCUSSION OF WORK PERFORMED BY ALL PARTIES

Please see the attached two publications:

reprints removed

- ▶ "Biosorption of uranium by *Pseudomonas aeruginosa* strain CSU: Characterization and comparison studies" (M. Z.-C. Hu, J. M. Norman, B. D. Faison, and M. E. Reeves)
- ▶ "Biosorption of uranium by *Pseudomonas aeruginosa* strain CSU immobilized in a novel matrix" (M. Z.-C. Hu and M. Reeves)

INVENTIONS (MADE OR REPORTED)

Inventions made in the course of this work are described in ORNL Invention Disclosure ESID 1690-x, s-83, 311. A patent covering this information was filed in March, 1997.

COMMERCIALIZATION POSSIBILITIES

Our CRADA partner, who had originally expressed interest in commercializing the technology developed under this CRADA, ultimately lost interest in this possibility.

PLANS FOR FUTURE COLLABORATION

None.

CONCLUSIONS

Work performed under this CRADA indicated the feasibility of a bioengineering design for the treatment of uranium-contaminated waters, including both ground and surface water. *Pseudomonas aeruginosa*, which had previously been implicated in the scavenging of uranyl ion from dilute solution, was shown to be highly sorptive toward uranium relative to other commercial (bio)sorbents, particularly in the presence of other dissolved metals. The process was shown to be sensitive to pH but not to cell viability, and to mimic ferric ion sorption. It may be concluded that a two-stage process entailing removal of iron, followed by uranium, by the *P. aeruginosa* sorbent would achieve efficient treatment of acidic leachates. Moreover, it was demonstrated that the sorbent could be mass-produced in immobilized form within a novel polyurethane hydrogel. This rugged biosorbent material could be rapidly fabricated, utilized within traditional batch or flow-through systems, regenerated, and reused indefinitely. Its behavior was readily modeled, allowing the design of large-scale systems. Preliminary calculations showed that a process based on this material would be competitive with traditional uranium-removal processes. Unfortunately, the planned pilot-scale demonstration was hampered by lack of funding. It may be concluded that this work would lend itself to future field demonstrations at sites in the U.S. or elsewhere.

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