

Application of Biosorption for Rare Earth Recovery from Geothermal Brines

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ABSTRACT

The development of new methodologies that enable the economic and sustainable extraction of rare earth elements (REEs) from non-traditional feedstocks such as geofluids can help alleviate REE supply vulnerability and diversify the global supply chain. Using bioengineered rare earth-adsorbing bacteria, we have developed a biosorption technology that can be used for extracting rare earth elements from geofluids. Through selective adsorption of REEs on the cell surface, we observed effective REE recovery in a temperature-dependent manner. As a first step towards developing a modular, scalable extraction scheme, we examined continuous a flow-through system relying on immobilized microbes via biofilm formation or cell encapsulation. The initial performance with geofluids is presented and discussed. Besides REEs, the concept of biosorption using immobilized biomass can also be applied for effective recovery of other critical metals from geofluids.

1. INTRODUCTION

Rare earth elements (REEs) are critical components in automotive and industrial catalysts, permanent magnets, electronics, and defense technologies. However, the supply of REEs is uncertain and potentially at risk globally. The development of new methodologies that enable economic and sustainable REE extraction is urgently needed. Biosorption has gained interest in recent years as a potential cost-effective and sustainable method for REE recovery. The high binding affinity of bacterial cell surfaces for REEs relative to most non-REEs permits selective binding of these valuable metals from low-grade feedstocks when the concentrating of non-REEs are much higher than those of REEs.¹⁻⁴ In addition, cell surfaces can withstand multiple cycles of adsorption and desorption, enabling reuse of biomass.⁵ Furthermore, the biosorption process is not expected to contribute hazardous chemical wastes, unlike conventional solvent extraction methods.⁶⁻⁷ Overall, microbial surface adsorption could present a clean and effective means for REE recovery.

Geofluids are abundant, REE-containing feedstocks that are currently being investigated as a potential source of REEs.^{1-2, 8-9} Although they are relatively low in REE concentrations (sub-ppb to low-ppm levels¹⁰), geothermal fluids have the advantage of requiring minimal pretreatment prior to biosorption, unlike other solid feedstocks such as ion adsorption clays, mine tailings, and fly ash, where chemical leaching is generally required.^{9, 11-12} The geochemical characteristics of geofluids vary greatly, motivating a deeper investigation of their impact on REE biosorption. In particular, the temperature of geofluids varies significantly, and previous studies have demonstrated that increasing temperature can lead to increased REE adsorption onto organic surfaces.¹³⁻¹⁵ To alleviate fouling and other complications associated with fluid cooling, rare earth recovery at higher than ambient temperatures may be advantageous. This motivated our investigation into the temperature effect on REE biosorption.

To further improve the adsorption capacity and selectivity of bacterial cell surface for REEs, we have previously bioengineered *Caulobacter crescentus*⁵ and *Escherichia coli*¹² to express lanthanide binding tags (LBTs) on the cell surface. Our strategy relies on environmentally safe microorganisms, and combines native microbial cell surface features with advanced bioengineering to increase microbes' resilience and extraction capabilities. Here, we investigate the REE adsorption performance of the bioengineered microbes under conditions characteristic of geofluids. Furthermore, to streamline REE recovery in a flow-through system, we developed a cell immobilization method that allow for column chromatography studies. Results define the geochemical conditions and process engineering factors that are important for REE biosorption, and provide key information for high-performance REE recovery from geofluids.

3. APPLICATION OF BIOSORPTION FOR REE EXTRACTION

3.1 Brine selection and REE speciation analysis

Geofluids from Great Salt Lake (GSL) and Blue Mountain brine (BMB) were obtained from Idaho National Lab and AltaRock Energy Inc, respectively. The Great Salt Lake (Utah, USA) is a terminal lake, which due to evaporation, contains among the highest total dissolved solids commonly found in natural geofluids. GSL brine has been characterized previously by Hari Neupane at Idaho National Lab. We conducted aqueous speciation analyses of natural GSL and mock solutions spiked with 1 or 100 ppb Tb. The GSL speciation (**Figure 1A**) aligns with our basic speciation expectations that strong carbonate complexes would form at neutral to alkaline pH. Although we expected strong aqueous complexes with fluorides at neutral pH and with chlorides and hydroxides at lower pH, the dominant species in the lower to circumneutral pH range is present as Tb³⁺, a free ion. Using the limited phases currently present in the modeling program PHREEQC's database, we observed saturation indices for a few Tb phases (**Figure 1B**). Notably, Tb(OH)₃ has a saturation index that exceeds 0 at pH ~ 8.7, suggesting a potential for precipitation of this phase at higher pH values. The fluoride and carbonate complexes, however, maintain a saturation index below 0. We thus do not expect precipitation of those phases. Therefore, although GSL has very high salts, this solution matrix allows high REE solubility at pH 4-6, a pH range that is amenable for biosorption.

Blue Mountain brine (BMB) were sampled in the Blue Mountain region (Nevada, USA) by AltaRock Energy Inc (WA, USA). It contains no detectable REEs using ICP-MS and REEs were later spiked in and used for biosorption experiments. Unlike GSL, REE solubility in the natural BMB is limited, with empirically determined ~90% solubility at 10 ppb Tb spike (pH 6) and ~70% solubility at 1000 ppb Tb spike (pH 6). Unfortunately, the available information of major cations and anions concentrations did not indicate the exact factor(s) that limit REE solubility. Given the low solubility of REE-phosphate complexes, we speculate that low-level phosphate content in BMB controls REE solubility at pH 6.

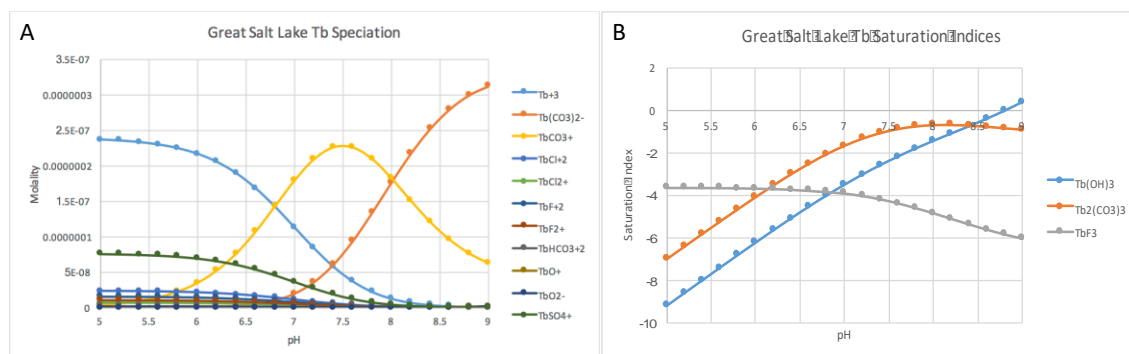


Figure 1. REE speciation with natural Great Salt Lake (GSL) spiked with 1 μM concentration of Tb (A) and saturation indices for Tb phases (B).

3.2 Temperature effect on REE biosorption

Given that minimizing brine cooling alleviates silicate fouling, performing mineral recovery from geothermal brines at higher than ambient temperatures could be beneficial. Accordingly, we tested how REE adsorption performance changes with increasing temperature. As shown in **Figure 2A**, an increase in Tb adsorption was observed with increasing temperature in both native and LBT-engineered strains across the temperature range tested (20-100°C), despite cell death occurred at elevated temperatures. To further examine whether the increase in REE biosorption is caused by a temporary change in thermodynamics or a permanent change in cell surface structure due to heating, we conducted the following control experiments. With GSL synthetic solution, we spiked in Tb at high concentrations to ensure under-saturation of the cell surface binding sites. With one sample, we conducted the REE adsorption experiment at room temperature as usual. With a 2nd sample, we conducted the biosorption reaction at 70°C in a heated water bath. And a 3rd sample, we heated the cells to 70°C for half hour and cooled the cells down to room temperature before conducting the rare earth biosorption experiment (**Figure 2B**). As observed previously, rare earth adsorption increased at elevated temperature (comparing column 1 and 2, Figure 2B). Given that the sample No. 3, the heated and cooled sample, showed similar amount of adsorption as the room temperature control (column 1), and is significantly lower than adsorption at higher temperature (column 2), we conclude the temperature effect on rare earth adsorption is largely reversible rather than a permanent feature. Consistently, changes in temperature have been shown to directly impact the thermodynamics of metal complexation by surface ligands.^{16, 17} It can be attributed to changes in metal-bacteria stability constants with temperature, caused by a reversible increase in the enthalpy of REE inner sphere complexation with cell surface functional groups.¹⁸

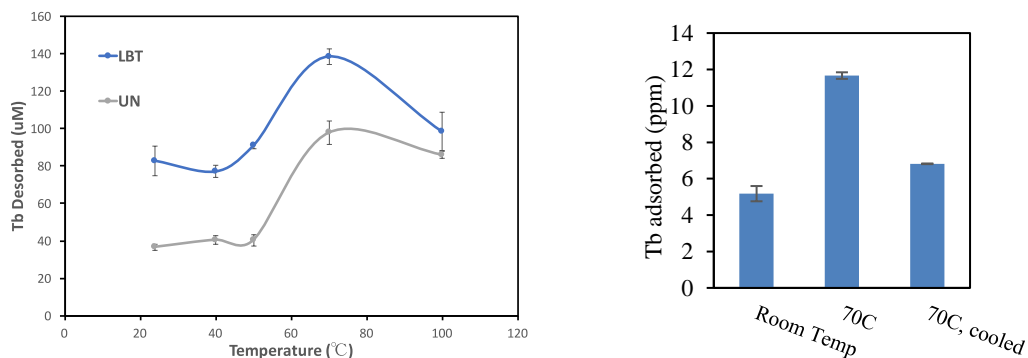


Figure 2. (A) Both *E. coli* LBT and non-LBT (UN) strains showed an increase in Tb adsorption with increasing temperature up to 70 $^{\circ}\text{C}$, with adsorption capacity remaining roughly constant between 70-100 $^{\circ}\text{C}$. Differences in adsorption capacity between LBT and non-LBT strains become smaller with increasing temperature. (B) Examine the reversibility of the temperature effect on REE adsorption. 1st column: Tb adsorption at room temperature; 2nd column: Tb adsorption increases at elevated temperature (70 $^{\circ}\text{C}$); 3rd column: Tb adsorption at room temperature (RT) with heated (to 70 $^{\circ}\text{C}$) and cooled (to RT) cells, showed that the temperature effect on REE adsorption is reversible.

3.3 Selection of eluents

Given its potential energy/cost benefit, we had initially intended to test the efficacy of high temperature/heat as a strategy for REE desorption. However, based on the observation of increased REE biosorption with temperature as shown in Figure 2, it is clear that elevated temperature will not be effective for REE desorption/recovery. We tested and compared a few common metal-chelating ligands (e.g., citrate, oxalate, and bicarbonate) for rare earth desorption, which are known to exhibit medium/strong metal chelating abilities. **Figure 3** showed that citrate (pH 6) is the most efficient eluent, desorbing high amount of the adsorbed REEs at concentrations below 5 mM. Higher concentrations of oxalate and bicarbonate are required for 100% desorption.

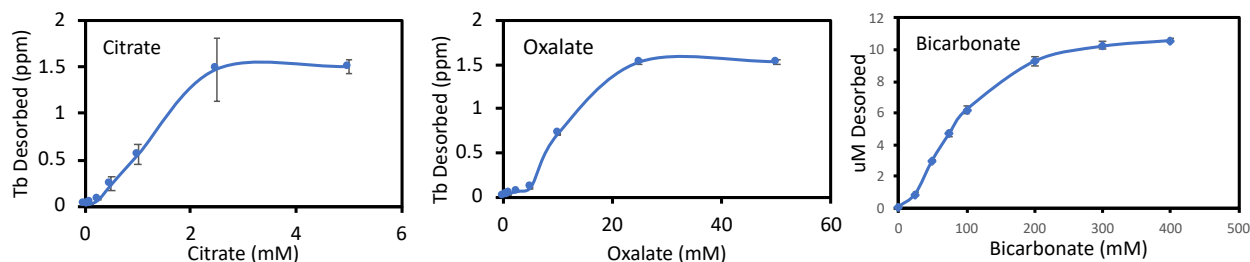


Figure 3. Comparison of REE desorption efficacy of different chemicals including citrate (pH 6), oxalate (pH 6) and bicarbonate (pH 7.5).

3.4 Cell immobilization for flow-through REE recovery

Cell immobilization is a critical step towards a flow-through operation as it enables facile separation of cells from geofluids upon biosorption. To this end, we characterized the biosorption efficacy of two different immobilization platforms, biofilm formation on solid support materials, and cell encapsulation within a polymer matrix.

3.4.1 Caulobacter biofilm on polystyrene well-plates. *Caulobacter crescentus* forms robust biofilms on a variety of surfaces, making biofilm formation an attractive immobilization mechanism. As a first step to develop a biofilm-based REE adsorption platform, the biofilm formation efficacy and temperature stability of LBT-displayed *C. crescentus* cells was determined (**Figure 4**). First of all, we observed that LBT-displayed cells achieved a biofilm density that was indistinguishable from native *C. crescentus* cells. Furthermore, the biofilm density was not reduced by incubation at 70°C, confirming the thermostability of *C. crescentus* biofilms. We next tested the REE biosorption performance of *Caulobacter* biofilms grown on polystyrene support material by exposing pre-formed biofilms to a Tb-containing solution. Given the increased REE adsorption at higher temperature observed with planktonic cells, the biofilm adsorption experiment was performed at both room temperature and 70 °C (**Figure 4A**). A 2-fold increase in REE adsorption with dLBT biofilms compared to the biofilms produced with *Caulobacter* lacking LBT was observed. Furthermore, compared to room temperature, an additional ~3 to 4-fold increase in Tb adsorption was observed with both LBT-displayed and control strains at 70 °C, consistent with results exhibited by planktonic cells (**Figure 2A**). We estimate that biofilms adsorbed ~18-22 $\mu\text{moles Tb}/\text{m}^2$ in this immobilization format, exceeding the assumption of 5 $\mu\text{moles Tb}/\text{m}^2$ used in the prior techno-economic analysis.¹⁹ The efficacy of *C. crescentus* biofilms to extract REEs from relevant geothermal fluid feedstocks was next tested using Blue Mountain geothermal fluid (BMB) spiked with 1 ppm Tb. As shown in **Figure 4B**, biofilms of LBT-displayed cells adsorb Tb at ~9 $\mu\text{moles}/\text{m}^2$, with contaminating metals adsorbed below the detection limit.

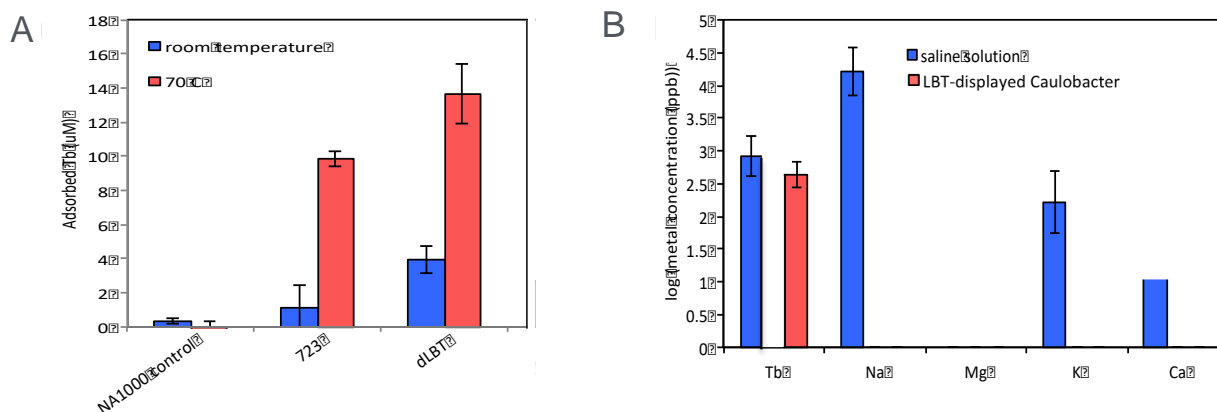


Figure 4. Biofilm adsorption capacity test with polystyrene 24-well plates. Control and LBT-displayed *Caulobacter* biofilms were pre-formed in the well plates and used for REE adsorption assays. (A) Adsorption experiments were performed in MES buffered (pH 6) solution with 15 $\mu\text{M TbCl}_3$ for 30 min, incubated at room temperature or 70°C. (B) Metal adsorption from BMB spiked with 1 ppm Tb.

We next focused on identifying biofilm support materials that facilitate a scalable flow-through operation. Mutag BioChips were selected as cell immobilization media, given their widespread application for seeding bacterial biofilms in wastewater treatment plants. Mutag BioChips™ have a high surface area to volume ratio ($> 4,000 \text{ m}^2/\text{m}^3$) and support high-density biofilm growth. As expected, Mutag BioChips were successfully colonized with LBT-displayed *Caulobacter* cells, yielding $\sim 1 \text{ mg}$ dry weight cells per chip. (Figure 5). The REE adsorption capacity of biofilm-coated Mutag chips was determined by incubating chips in a synthetic saline solution spiked with Nd. An adsorption capacity of $\sim 30 \mu\text{g Nd}$ per chip was observed, which translates to $\sim 7.5 \text{ g Nd}/\text{m}^3$ of adsorbent. Importantly, the per cell adsorption capacity of the biofilm chips was in good agreement with planktonic cells ($\sim 32 \text{ mg Nd}/\text{gram}$ of dry cell weight in biofilm compared to $\sim 29 \text{ mg Tb}/\text{g}$ dry cell weight for planktonic cells), suggesting that the LBT and native cell surface functional groups of immobilized cells are accessible to Nd biosorption. This also equates to an adsorption capacity of $\sim 87 \text{ micromoles}/\text{m}^2$ (area of cell surface).

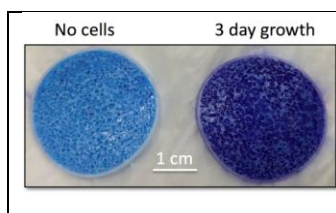


Figure 5. *Caulobacter* biofilms formed on Mutag BioChips. Successful biofilm colonization was confirmed using the crystal violet assay, with an estimate of $\sim 1 \text{ mg}$ dry cell weight attached per chip.

3.4.2 Microbe encapsulation. Cell encapsulation is another cell immobilization strategy that we tested. Microbe encapsulated polymer beads were synthesized and packed into a column as the stationary phase, and REE adsorption/desorption was performed using the packed column (Figure 6A). Approximately $\sim 2.8 \text{ ml}$ of microbe beads were loaded into a 3 mL column, and REE-containing solution was passed through the column at a flow rate of $0.4 \text{ ml}/\text{min}$. Desorption was performed by passing through 10-20 ml citrate solution (10 mM , $\text{pH } 6$). Three adsorption/desorption experiments were performed with the same column with a washing step (10 mM MES , $\text{pH } 6$) performed in between runs (Figure 6B, C). To test the column reusability, a feed solution (500 mL) that contained 1 ppm Nd was used in the first 2 rounds and feed stock that contained 100 ppb Nd ($\sim 1100 \text{ ml}$) was used in the third round. Results indicated greater than 80% REE recovery (98% with the 100-ppb feed, Figure 6C) in all 3 runs with no reduction in performance observed over time. By using a smaller volume of citrate to desorb Nd from the column, the Nd concentration in the eluent was effectively concentrated by 20-, 22-, and 112-fold after the 3 runs relative to the feed solutions, respectively.

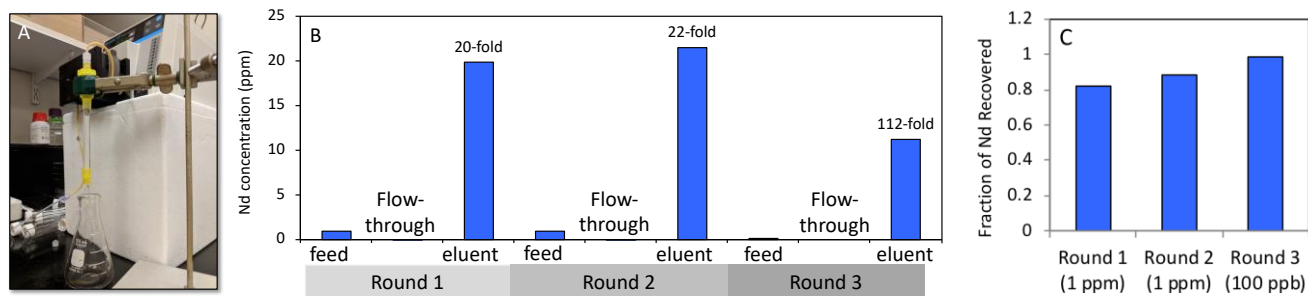


Figure 6. (A) column setup for REE recovery under flow-through. (B) Nd concentration in the initial feed, flow through, and eluent for 3 consecutive adsorption/desorption cycles. (C) REE recovery efficiency of more than 80% observed in all 3 runs.

4. CONCLUSIONS AND PERSPECTIVES

Clearly, two cell immobilization strategies described have different features and require different process schemes to enable rare earth recovery under flow-through. The biofilm-based cell immobilization, using the Mutag BioChips or other biofilm carriers, has been primarily developed and optimized for waste water treatment plants, removing organic contaminants through biological activities of biofilms. For metal recovery purpose, pre-seeding of the microbes is required. The seeding efficiency, i.e., the ratio of the attached cells vs planktonic cells, is relatively low and further improvement of cell seeding is required. Biofilm stability is another factor that is less important for wastewater treatment, but has become critical for metal recovery application, given biofilms detached would pose a competing effect on metal recovery. Nutrient starvation is known to promote biofilm detachment and long-term stability of inactive biofilms is not well known. In terms of application platform for biofilm-based cell immobilization, fluidic-bed bioreactors such as air-lift bioreactors are expected to be well suited.

Compared to biofilm formation, cell encapsulation in polymer matrix depends less on biological factors and thus appears to be more predictable in terms of performance and stability. The polymer matrix properties such as rigidity and pore size can be adjusted depending on needs. Cell encapsulation efficiency is high, with little cell loss during the microbe bead synthesis process. The beads are stable in storage for months, and cell preservation by lyophilization likely extends the shelf life further. Compared to biofilms that have cells exposed on the surface, encapsulation may provide more protection to the imbedded microbes from environmental perturbations, increasing biomass lifetime, allowing repeated/continuous use, and lower production cost. In terms of application platform, a fixed-bed bioreactor in the form of ion-exchange columns would probably be the most straightforward, although batch scale operation with 'loose' beads may also be suitable, especially for feed solutions with high solid loads. Ongoing work focuses on more quantitative comparisons of rare earth recovery efficiency of these two cell immobilization strategies and bioreactor performance, developing a scalable process for rare earth recovery from geofluids.

Once developed successfully, biosorption using the REE-adsorbing microbes could be an innovative, cost-effective, and ecofriendly technology to sequester and recover REE from geofluids. It is expected to offer the same process efficiency as seen previously

in heavy metal bioremediation and permits a method specifically designed for feedstocks with low REE content. Combined with other mineral extraction processes (Li/Mn/Zn), the development of REE biosorption from geofluids will add valuable revenues to existing geothermal operations and diversify REE supply chain.

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