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A Biotechnology Application for Rare Earth Extraction from Geothermal Brines

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ABSTRACT

Using our bioengineered rare earth-adsorbing bacteria, we have developed a novel biosorption system for the extraction of rare earth elements (REE) from low-grade sources such as geothermal brines. We have demonstrated the proof of concept for this process through competitive REE adsorption and desorption in batch mode, and now a continuous flow system relying on immobilized microbes on abiotic surfaces is currently under development at the laboratory scale. Synthetic geothermal brines spiked with REE have been tested to assess REE biosorption performance with promising results. Future work will include performance tests with minimally pretreated (temperature and pH) geothermal brine collected from Blue Mountain (NV), Salton Sea (CA), and other selected geothermal sites.

1. INTRODUCTION

There is an ever-increasing demand for REE in renewable energy and emerging green technologies, such as wind turbines, solar panels, and hybrid/electric vehicle batteries. However, the current uncertainty in the supply of REE hinders development of these technologies in the U.S. and Europe. Five REE (Tb, Dy, Eu, Nd, and Y) in particular have been highlighted by the U.S. Department of Energy for both their supply vulnerability and criticality to the development of emerging clean energy technologies (DOE 2011).

Due to its abundance and availability, geothermal brines represent an inexpensive and attractive mineral source that could be exploited for REE extraction (Finster et al. 2015; Wood 2001). With the global increase in geothermal energy and the exploration of unconventional oil and gas resources, large volumes of geothermal fluid are being generated. The characteristic features of these brines in terms of REE content, chemistry, and minerology are highly variable depending on location and geochemical conditions, ranging in concentration from ppb to ppm (Table 1). Due to the lack of high yield or low cost methods, no operations currently exist for extracting REE from geothermal brines. The low REE content and high salt concentrations in a typical geothermal brine prohibit the use of conventional REE-extraction approaches at an industrial scale. Development of technologies for recovery of valuable byproducts such as REE from geothermal brine could improve the economics of geothermal plants while diversifying critical material resources.

Table 1: A brief survey of REE content in geothermal systems.

Location/REE (ppb)	Eu	Nd	Dy	Yb	Total	Reference
Sangan Thermal Spring, Iran	27.5	625	61	23.4	3183.8	(Shakeri et al. 2015)
Zhenzhu Spring, China	0.033	3.632	0.853	1.013	39.1	(Zhang et al. 2016)
Obuki Hot Spring, Japan	2.63	47	11.3	5.87	220.4	(Sanada et al. 2006)
Bizovka Spring, Croatia	6.41	0.118	0.03	5.54	16.9	(Fiket et al. 2015)
Bigelow Hot Springs, Oregon	0.034	0.599	0.117	0.058	2.9	(Wood 2001)

[a]Total REE include the 15 lanthanides only.

2. REE BIOSORPTION RATIONALE

Microbially mediated surface adsorption (biosorption) has received growing attention in recent years as a cost-effective and ecofriendly approach for metal processing (Zhuang et al. 2015; Fein, Martin, and Wightman 2001; Mejare and Bulow 2001). Various metals, including Cd, Hg, Pb, U, and the REE, can be removed and recovered from solution by adsorbing onto the cell surface of microorganisms (Hennebel et al. 2015; Texier, Andres, and Le Cloirec 1999). REE, most commonly present at a +3 redox state, have a high affinity for phosphate and carboxyl groups that are highly abundant on cell surfaces (Jiang et al. 2012), making biosorption particularly relevant for REE. Microbes are economical and ecofriendly biosorbents due to their small sizes and rapid growth rates, facilitating rapid adaptation to a wide range of environmental conditions. Expanding upon native microbes' metal adsorption capacities, bioengineering can greatly enhance the capacity and specificity of biosorbents to targeted metals (Wei et al. 2014). For example, overexpression of metal-binding peptides on the surfaces of *E. coli* cells facilitate specific extraction of a target metal (e.g., Au) while minimizing metal toxicity to host cells (Zhuang et al. 2015; Hennebel et al. 2015).

Due to the low concentrations of REE in geothermal brines compared to conventional REE ores, a large quantity of feedstock need to be processed in order to provide a viable REE supply. Therefore, process engineering and system scalability to ensure efficient REE extraction are critical steps to permit a REE extraction technology to be adopted by the industry. Development of a continuous flow system incorporating immobilized cells represents a key step for scaling-up, as it allows for complete separation of REE ions from the aqueous solution in a single step. Our bioengineered REE-adsorbing bacterium *Caulobacter crescentus* has an intrinsic ability to form stable and uniform biofilms on solid surfaces (Berne et al. 2013), a distinct feature that can be exploited for cell immobilization via surface attachment.

3. APPLICATON OF BIOADSORPTION FOR REE EXTRACTION

3.1 Bioengineer of Microbes

REE are not essential metals for life, and in fact very little is known about their function in any biological system (Pol et al. 2013). Despite this, previous efforts in protein engineering have led to the discovery of lanthanide binding tags (LBTs), which are short peptides (~15 amino acids) that bind to REE with high affinity and specificity (Nitz et al. 2004). For genetic engineering of REE-adsorbing microbes, the host microbe that we have chosen is *Caulobacter crescentus*, an environmentally safe bacterium that has a high tolerance to heavy metals and can survive in very low-nutrient environments (Hu et al. 2005). Additionally, *Caulobacter* is an ideal biological system for metal adsorption due to its encapsulation by an S-layer that is highly amenable to bioengineering (Amat et al. 2010). These high-density S-layer proteins (~40,000 copies/cell) provide anchors for the display of LBTs, allowing for an inexpensive and scalable source of LBTs for REE adsorption. Accordingly, taking advantage of the excellent LBT-REE binding properties, genetic manipulation has produced a bioengineered strain that is able to produce and display LBT peptides on its surface during cell replication. The LBT tags can bind to metal atoms with 1,000 times greater affinity for rare earths than other metals, allowing specific adsorption of REE even in the presence of relatively high concentrations of other competing metals (Park et al. 2016). Once the cells have adsorbed the REE, we apply a REE stripping solution (5 mM sodium citrate, pH 6) that allows effective desorption and recovery the REE from the cell surface and, in doing so, makes the biomass available for reuse (Figure 1).

Conventional REE extraction approaches, particularly those which generally emphasize hydrometallurgy via solvent extraction, are chemically/energy intensive, and pose severe environmental burdens and therefore are not feasible for low-grade feedstocks. In contrast, the biosorption technology was specifically designed for low-grade feedstocks to extract REE in an economic and ecofriendly manner. The use of biosorbents for metal extraction from aqueous systems is at least an order of magnitude cheaper than traditional technologies and minimizes chemical waste generation (Davis, Volesky, and Mucci 2003). We expect that this cost-effective and ecofriendly alternative for REE refinement, once optimized, will out-perform conventional approaches.

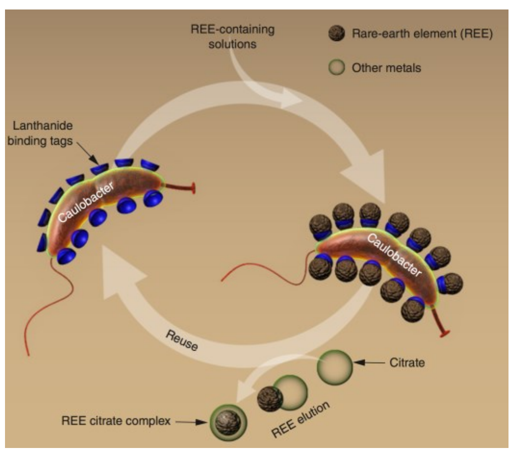

Figure 1: An urgent need exists for new approaches to efficiently extract and recover rare earth from low-grade feedstocks including geothermal brines. As one step towards this goal, we have genetically engineered the bacteria *Caulobacter crescentus* and *E. coli* to selectively adsorb rare earth ions onto their cell surfaces. The adsorbed rare earths can be recovered using a citrate solution and the microbes can be recycled and reused.

3.2 REE Biosorption Performance

Our engineered REE-adsorbing microbes showed remarkably superior adsorption performance to the non-engineered microbes, especially under high salt conditions. As shown in Figure 2, in a synthetic high-salt mock solution spiked with Tb, the engineered strains adsorbed 97% to 99% of the total REE, while the non-engineered bacteria were much less effective. The much improved REE adsorption capacity in the bioengineered cells makes these microbes valuable agents for REE extraction. Besides the high capacity for REE adsorption, the bioengineered cells are also highly selective towards REE compared to other metals (Park et al. 2016). Besides mock solutions made in the laboratory, we also demonstrated the feasibility of REE extraction with sediment core samples collected from a prospective REE mine (Bull Hill, WY) (Figure 3), suggesting the practicality to work with real world samples. To further demonstrate the applicability to geothermal brine, we tested the REE adsorption performance with a synthetic solution matrix that mimics the geothermal brine at Blue Mountain (NV), with an added Tb spike. As shown in Figure 4, the increase in luminescence (indicative of REE-LBT binding, (Nitz et al. 2004)) with increasing Tb concentration suggests specific Tb adsorption on REE-absorbing bacteria. In addition, we observed no reduction in REE adsorption capacity following citrate elution, enabling consecutive adsorption/desorption cycles without loss of adsorption capacity or cell viability (tested through three cycles, (Park et al. 2016)). It is worth noting that REE biosorption capability does not depend on cell viability; dead cells (as long as cell structure is intact) exhibit similar adsorption performance to live cells. Our results demonstrate a rapid, efficient, and reversible process for REE adsorption using our bioengineered REE adsorbing microbes that holds potential for industrial application.

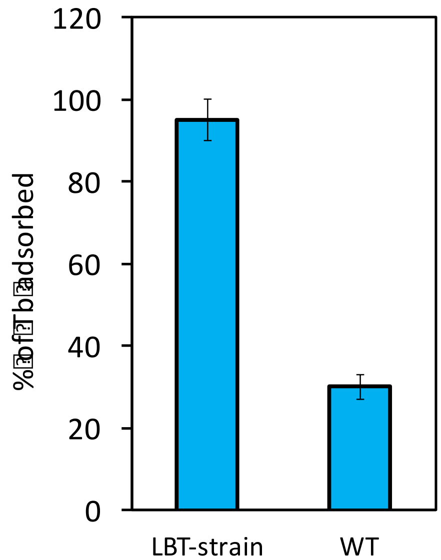

Figure 2: Enhanced REE adsorption capacity in our bioengineered REE adsorbing strain of Caulobacter. Comparison of Tb3+ adsorption capacity between the bioengineered (LBT-strain) and wild type strains (WT) indicates that our bioengineering effort resulted in an increase in Tb3+ loading capacity by > 3-fold, reaching 95% efficiency. Experiment was performed in the presence of 150 mM Ca2+.

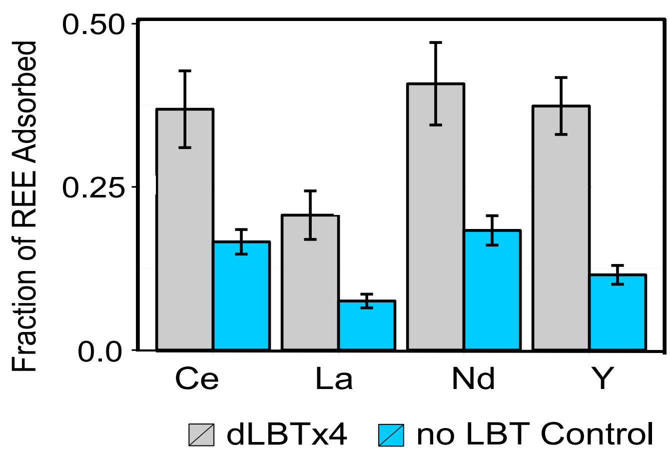

Figure 3: REE extraction from a sediment core sample collected from a prospective rare earth mine at Bull Hill, WY. Our bioengineered strain (dLBTx4) showed significant enhancement in REE adsorption compared to the wild type (no LBT Control) for all major REE present. The concentration of Y (0.02 mg/100 mg sediment) is present at ~100 fold lower concentration than Ce (1.7 mg/100 mg sediment), highlighting the wide range of effectiveness of REE adsorption.

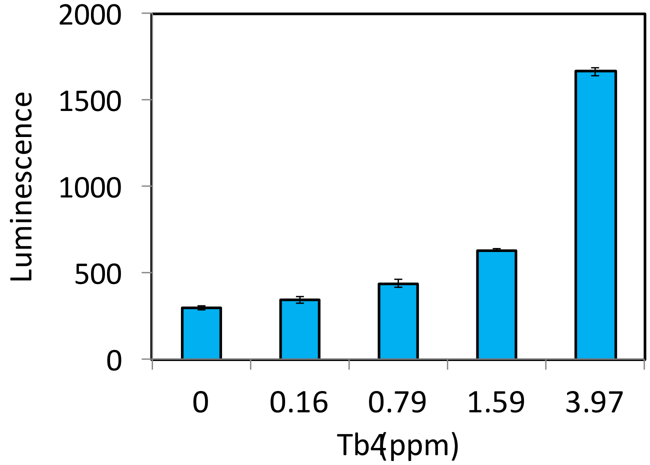

Figure 4: Batch adsorption isotherm of REE-adsorbing Caulobacter equilibrated in a solution matrix that mimics the geothermal brine at the Blue Mountain (NV) with an added Tb spike. The increase in luminescence with increasing Tb concentration suggests specific Tb adsorption onto the REE-absorbing bacteria.

3.3 Cell immobilization and Selection of Adsorption Media

To improve the scalability of the REE-adsorption system toward industrial application, our current efforts focus on adapting the batch scale adsorption operation to a continuous flow system through cell immobilization. Cell immobilization in a flow through system allows the separation of the REE adsorbent from the rest of the solution without requiring centrifugation or a column separation step. Three types of adsorption media for cell immobilization are currently under investigation, including biofilm formation, cell encapsulation, and carbon nanotube embedded membranes. Cell immobilization based on one of these techniques in a flow through setup will facilitate system scale up and industry adoption.

3.3.1 Cell immobilization via biofilm formation

A biofilm is a layer of microorganisms that are adhered to a surface. Biofilms are ubiquitous and nearly every species of microorganism have mechanisms by which they can adhere to surfaces and to each other. *Caulobacter* uses a distinctive feature to self-immobilize and form uniform, high-density biofilms on supported solid surfaces; it has a strongly adhesive organelle, a holdfast that is present at the distal tip of the stalk. 3D mushroom-like structures are observed to form interspersed with monolayer biofilms. These 3D structures can promote cell detachment, cause clogging and disruption of solution diffusion and transport (Entcheva-Dimitrov and Spormann 2004), features that are undesirable for REE adsorption. To overcome this, a *flgH* mutant (that cannot make a functional flagellum) has been shown to form mono-layer biofilm without the extensive, mushroom-like structure formation. Ongoing effort focuses on cell attachment and monolayer biofilm formation using the *flgH* mutant attached to different supporting materials (e.g., glass and glass beads), followed by REE adsorption performance testing (Figure 5).

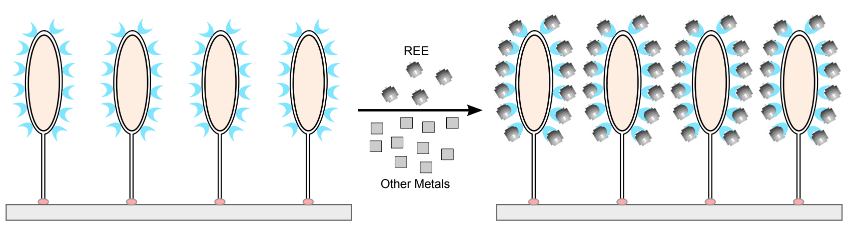

Figure 5: A schematic showing of a REE-adsorbing Caulobacter biofilm, formed on a supporting surface, which can be used to sequester REE from solution. Bioengineered REE-adsorbing Caulobacter not only selectively sequester dissolved REE but also form a monolayer biofilm using their distinctive holdfasts, enabling a single step for REE extraction.

3.3.2 Cell immobilization through encapsulation

Cell encapsulation by polymer materials is another commonly used method for cell immobilization. These polymer supports have been used for a wide range of applications because of their highly tunable mechanical and chemical properties, such as their easy and versatile formation, crosslinkable nature, strength, and wide variety of chemical compositions (Flickinger et al. 2007; Blanchette et al. 2016). In addition, their high permeability, large surface area, and non-toxicity make them ideal substrates for cell encapsulation for metal adsorption. As such, various matrix materials have been used to embed microbes for the separation of metal ions from solution (Xu et al. 2015; Vannela and Verma 2006).

Currently we are exploring a few of commonly used polymer materials for embedding the REE-adsorbing microbes. These polymers include alginate, polyethylene glycol (PEG), and polyacrylamide gel (PAG). For cell embedding within alginate, concentrated and washed REE-adsorbing cells were resuspended in aqueous sodium alginate and injected through a syringe into a calcium chloride solution as described previously (Singh et al. 1989). Spherical beads of roughly 2- mm in diameter were formed, washed, and tested in a REE biosorption experiment with a mock Tb solution. Control beads were prepared using same procedure without microbes. Preliminary results revealed high background REE adsorption even without cell loading, affecting the purity of the recovered REE. Alginate is known to have extensive binding capability towards a wide range of metal ions including REE (Yu et al. 2013; Kwiatkowska-Marks, Wojcik, and Kopinski 2011; Xu et al. 2015), limiting their application for REE extraction due to the high concentrations of contaminating metals expected to be present in target feedstocks such as geothermal brine. The applicability and performance tests with PEG and PAG polymers are currently under investigation.

It is worth noting that compared to cell attachment through biofilm formation on supporting surfaces, cell encapsulation within polymers may slow down REE adsorption kinetics. Since microbes (and thus the effective cell surface) are encapsulated within the polymer matrix, REE adsorption kinetics may become limited by the diffusion rate of REE within the matrix. One way to alleviate the kinetic issues is to decrease the size/dimension of the encapsulated particles. Besides the 1-5 mm range of encapsulated beads, smaller sizes in the range of 100-500 µm can be synthesized by a microfluidic setup (Martinez et al. 2012; Ye et al. 2010; Teh et al. 2008), which is also part of our ongoing work.

3.3.3 Cell immobilization through synthesis of carbon nanotube/bacteria composite membrane

Another platform for cell immobilization focuses on the synthesis and fabrication of a carbon nanotube/microbe composite membrane. In 2004, Wu *et al*. (Wu et al. 2004) developed a facile strategy to prepare high quality CNT membranes by using a vacuum filtration method. The vacuum filtration approach increases the homogeneity of the produced nanotubes membrane by controlling the permeation rate. Due to the high aspect ratio of CNT, the interpenetrated nanotubes can easily form a network with excellent mechanical integrity, which is critical for many applications.[1] The thickness of a CNT membrane can be tuned based on specific requirements by adjusting the loading of CNT powders. Vacuum filtration has been extensively applied to the synthesis of one-or/and two-dimensional nanomaterials based membranes. The fabrication of two-dimensional molybdenum disulphide (MoS_2) based film is another example of this method (Acerce, Voiry, and Chhowalla 2015). Yet, to the best of our knowledge, there is no report of using this strategy to prepare CNT/microbe composite membranes. Functional bacteria such as rare earth extraction microbes can be easily inoculated within the three-dimensional CNT networks (Figure 6). This method offers flexibility in tuning the properties/performance of the film by varying the ratio of CNT to the microbes. The conductive CNT scaffold also allows electrical and electrochemical measurements of the trapped microbes. Our work in applying these CNT/microbe composite membranes is currently ongoing.

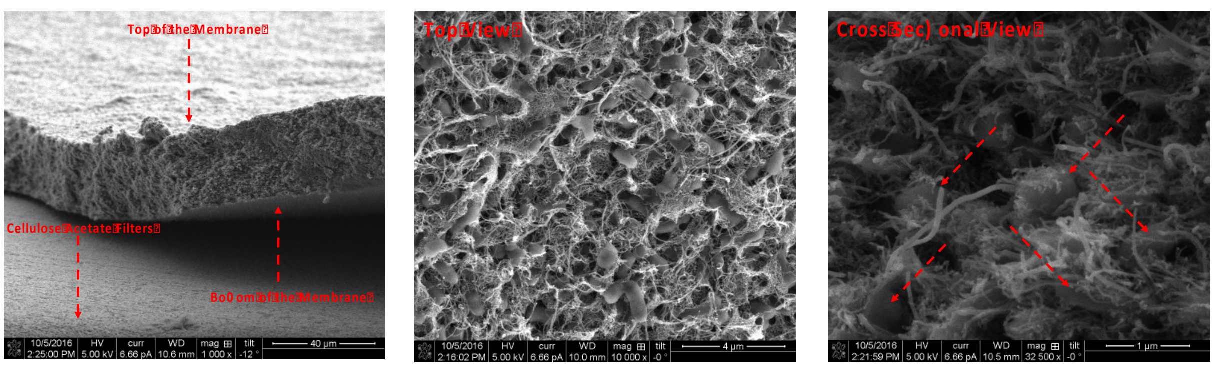

Figure 6: (left) Cellulose Acetate Filters (0.2 µm) Based Membrane. After bacteria fixation, the bacteria/CNT film detached from the cellulose acetate filters. The volume of the membrane is estimated about: 3.64 x 1010 µm3. (middle) From the top view of the cellulose acetate filters based membrane, we can see the bacteria are uniformly trapped in the CNT networks. (right) cross sectional view of this sample.

4. BIOREACTOR FOR REE ADSORPTION

Bioreactors are commonly employed to contain the REE-adsorbing media described in the previous section for REE adsorption under continuous flow. Bioreactors represent an efficient way of exploiting the REE-absorbing properties of our bioengineered microbes at an industrial scale. Bioreactors are operated with defined and controllable environmental parameters and allow improved contact between the biological agents and REE. Depending on the performance test results with the various adsorption media described in the previous section, bioreactors can be designed and fabricated accordingly. Various configurations such as packed bed and air-lift bioreactors and biosorptopn columns have been used for various metal adsorption applications. We expect that efficient extraction of high-purity REE can be achieved by establishing a cost-effective bioreactor design, an efficient workflow, and optimized operational conditions.

5. CONCLUSIONS

Biosorption using the bioengineered REE-adsorbing microbes could be an innovative, cost-effective, and ecofriendly technology to sequester and recover REE from low grade feedstocks such as geothermal brine. Our biosorption technology relies on environmentally safe microorganisms, and combines native microbial cell surface features with advanced bioengineering to increase microbes' resilience and extraction capabilities. This innovative biosorption technology 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. The development of REE extraction from geothermal brine will add valuable revenues to existing geothermal operations and diversify REE resources, without competing with the already limited high-value REE reserves in the U.S. We envision such a modular, versatile technology will also be applicable to extract other valuable metals (e.g., U, Sc, and V). The successful commercialization of this technology will provide the U.S. with a more secure source of clean technology source materials.

REFERENCES

Acerce, M., D. Voiry, and M. Chhowalla. 2015. 'Metallic 1T phase MoS2 nanosheets as supercapacitor electrode materials', *Nature Nanotechnology*, 10: 313-18.

Amat, F., L. R. Comolli, J. F. Nomellini, F. Moussavi, K. H. Downing, J. Smit, and M. Horowitz. 2010. 'Analysis of the Intact Surface Layer of Caulobacter crescentus by Cryo-Electron Tomography', *Journal of Bacteriology*, 192: 5855-65.

Berne, C., X. Ma, N. A. Licata, B. R. Neves, S. Setayeshgar, Y. V. Brun, and B. Dragnea. 2013. 'Physiochemical properties of Caulobacter crescentus holdfast: a localized bacterial adhesive', *J Phys Chem B*, 117: 10492-503.

Blanchette, C. D., J. M. Knipe, J. K. Stolaroff, J. R. DeOtte, J. S. Oakdale, A. Maiti, J. M. Lenhardt, S. Sirajuddin, A. C. Rosenzweig, and S. E. Baker. 2016. 'Printable enzyme-embedded materials for methane to methanol conversion', *Nature Communications*, 7.

Davis, T. A., B. Volesky, and A. Mucci. 2003. 'A review of the biochemistry of heavy metal biosorption by brown algae', *Water Res*, 37: 4311-30.

DOE. 2011. 'Critical Materials Strategy', http://www.energy.gov.

Entcheva-Dimitrov, P., and A. M. Spormann. 2004. 'Dynamics and control of biofilms of the oligotrophic bacterium Caulobacter crescentus', *J Bacteriol*, 186: 8254-66.

Fein, J. B., A. M. Martin, and P. G. Wightman. 2001. 'Metal adsorption onto bacterial surfaces: Development of a predictive approach', *Geochimica Et Cosmochimica Acta*, 65: 4267-73.

Fiket, Z., M. Rozmaric, M. Krmpotic, and B. Petrinec. 2015. 'Trace and Rare Earth Element Geochemistry of Croatian Thermal Waters', *International Journal of Environmental Research*, 9: 595-604.

Finster, M., C. Clark, J. Schroeder, and L. Martino. 2015. 'Geothermal produced fluids: Characteristics, treatment technologies, and management options', *Renewable & Sustainable Energy Reviews*, 50: 952-66.

Flickinger, M. C., J. L. Schottel, D. R. Bond, A. Aksan, and L. E. Scriven. 2007. 'Painting and printing living bacteria: Engineering nanoporous biocatalytic coatings to preserve microbial viability and intensify reactivity', *Biotechnology Progress*, 23: 2-17.

Hennebel, T., N. Boon, S. Maes, and M. Lenz. 2015. 'Biotechnologies for critical raw material recovery from primary and secondary sources: R&D priorities and future perspectives', *N Biotechnol*, 32: 121-7.

Hu, P., E. L. Brodie, Y. Suzuki, H. H. McAdams, and G. L. Andersen. 2005. 'Whole-genome transcriptional analysis of heavy metal stresses in Caulobacter crescentus', *Journal of Bacteriology*, 187: 8437-49.

Jiang, M. Y., T. Ohnuki, K. Tanaka, N. Kozai, E. Kamiishi, and S. Utsunomiya. 2012. 'Post-adsorption process of Yb phosphate nano-particle formation by Saccharomyces cerevisiae', *Geochimica Et Cosmochimica Acta*, 93: 30-46.

Kwiatkowska-Marks, S., M. J. Wojcik, and L. Kopinski. 2011. 'Biosorption of heavy metals on alginate beads', *Przemysl Chemiczny*, 90: 1924-30.

Martinez, C. J., J. W. Kim, C. W. Ye, I. Ortiz, A. C. Rowat, M. Marquez, and D. Weitz. 2012. 'A Microfluidic Approach to Encapsulate Living Cells in Uniform Alginate Hydrogel Microparticles', *Macromolecular Bioscience*, 12: 946-51.

Mejare, M., and L. Bulow. 2001. 'Metal-binding proteins and peptides in bioremediation and phytoremediation of heavy metals', *Trends in Biotechnology*, 19: 67-73.

Nitz, M., M. Sherawat, K. J. Franz, E. Peisach, K. N. Allen, and B. Imperiali. 2004. 'Structural origin of the high affinity of a chemically evolved lanthanide-binding peptide', *Angewandte Chemie-International Edition*, 43: 3682-85.

Park, D. M., D. W. Reed, M. C. Yung, A. Eslamimanesh, M. M. Lencka, A. Anderko, Y. Fujita, R. E. Riman, A. Navrotsky, and Y. Jiao. 2016. 'Bioadsorption of Rare Earth Elements through Cell Surface Display of Lanthanide Binding Tags', *Environ Sci Technol*.

Pol, A., T. R. Barends, A. Dietl, A. F. Khadem, J. Eygensteyn, M. S. Jetten, and H. J. Op den Camp. 2013. 'Rare earth metals are essential for methanotrophic life in volcanic mudpots', *Environmental microbiology*.

Sanada, T., N. Takamatsu, and Y. Yoshiike. 2006. 'Geochemical interpretation of long-term variations in rare earth element concentrations in acidic hot spring waters from the Tamagawa geothermal area, Japan', *Geothermics*, 35: 141-55.

Shakeri, A., S. Ghoreyshinia, B. Mehrabi, and M. Delavari. 2015. 'Rare earth elements geochemistry in springs from Taftan geothermal area SE Iran', *Journal of Volcanology and Geothermal Research*, 304: 49-61.

Singh, S. P., S. K. Verma, R. K. Singh, and P. K. Pandey. 1989. 'Copper Uptake by Free and Immobilized Cyanobacterium', *Fems Microbiology Letters*, 60: 193-96.

Teh, S. Y., R. Lin, L. H. Hung, and A. P. Lee. 2008. 'Droplet microfluidics', *Lab on a Chip*, 8: 198-220.

Texier, A. C., Y. Andres, and P. Le Cloirec. 1999. 'Selective biosorption of lanthanide (La, Eu, Yb) ions by Pseudomonas aeruginosa', *Environmental Science & Technology*, 33: 489-95.

Vannela, R., and S. K. Verma. 2006. 'Co2+, Cu2+, and Zn2+ accumulation by cyanobacterium Spirulina platensis', *Biotechnology Progress*, 22: 1282-93.

Wei, W., X. Liu, P. Sun, X. Wang, H. Zhu, M. Hong, Z. W. Mao, and J. Zhao. 2014. 'Simple Whole-Cell Biodetection and Bioremediation of Heavy Metals Based on an Engineered Lead-Specific Operon', *Environmental science & technology*.

Wood, S. A. 2001. 'BEHAVIOR OF RARE EARTH ELEMENTS IN GEOTHERMAL SYSTEMS: A NEW EXPLORATIONEXPLOITATION TOOL?', *DEPARTMENT OF ENERGY, GEOTHERMAL RESERVOIR TECHNOLOGY RESEARCH, DEVELOPMENT AND DEMONSTRATION*.

Wu, Z. C., Z. H. Chen, X. Du, J. M. Logan, J. Sippel, M. Nikolou, K. Kamaras, J. R. Reynolds, D. B. Tanner, A. F. Hebard, and A. G. Rinzler. 2004. 'Transparent, conductive carbon nanotube films', *Science*, 305: 1273-76.

Xu, S. X., Z. W. Wang, Y. Q. Gao, S. M. Zhang, and K. Wu. 2015. 'Adsorption of Rare Earths(III) Using an Efficient Sodium Alginate Hydrogel Cross-Linked with Poly-gamma-Glutamate', *Plos One*, 10.

Ye, C. W., A. Chen, P. Colombo, and C. Martinez. 2010. 'Ceramic microparticles and capsules via microfluidic processing of a preceramic polymer', *Journal of the Royal Society Interface*, 7: S461-S73.

Yu, K., J. Ho, E. McCandlish, B. Buckley, R. Patel, Z. B. Li, and N. C. Shapley. 2013. 'Copper ion adsorption by chitosan nanoparticles and alginate microparticles for water purification applications', *Colloids and Surfaces a-Physicochemical and Engineering Aspects*, 425: 31-41.

Zhang, Y. F., H. B. Tan, W. J. Zhang, H. Z. Wei, and T. Dong. 2016. 'Geochemical constraint on origin and evolution of solutes in geothermal springs in western Yunnan, China', *Chemie Der Erde-Geochemistry*, 76: 63-75.

Zhuang, W. Q., J. P. Fitts, C. M. Ajo-Franklin, S. Maes, L. Alvarez-Cohen, and T. Hennebel. 2015. 'Recovery of critical metals using biometallurgy', *Curr Opin Biotechnol*, 33: 327-35.