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Bioleaching of rare earth elements from waste phosphors and cracking catalysts

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ABSTRACT

Microbial cultures were evaluated for organic acid production and their potential utility for leaching of rare earth elements (REE) from retorted phosphor powder (RPP) and spent fluid catalytic cracking (FCC) catalyst. Two bacterial and one fungal strain were isolated from environmental and industrial materials known to contain REE and compared to the industrially important bacterium *Gluconobacter oxydans*. Gluconic acid was the predominant organic acid product identified in all of the cultures. Maximum REE leaching (49% of the total REE) from the FCC material was observed using cell-free culture supernatants of *G. oxydans*, with preferential recovery of lanthanum over cerium. The phosphor powder was more difficult to leach; only about 2% of the total REE was leached with *G. oxydans*. Leaching experiments with the RPP material indicated that the extent of REE solubilization was similar whether whole cell cultures or cell-free supernatants were used. Abiotic control experiments showed that increasing gluconic acid concentrations increased leaching efficiency; for example, total REE leaching from FCC catalyst increased from 24% to 45% when gluconic acid was increased from 10 mM to 90 mM. However, *G. oxydans* cell-free culture supernatants containing 10–15 mM gluconic acid were more effective than abiotically prepared leaching solutions with higher gluconic acid concentrations, suggesting that other exudate components were important too. Our results indicate that microorganisms producing gluconic and other organic acids can induce effective leaching of REE from waste materials, and that increasing organic acid production will improve recovery.

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1. Introduction

The recovery of rare earth elements (REE) from recyclable materials is an important component of the United States strategy for addressing anticipated future shortages of metals critical for our modern technological society (DOE, 2011). The REE neodymium, europium, terbium, dysprosium, and yttrium are used in everyday products such as computers, smartphones and lighting, and in advanced clean energy technologies such as hybrid cars and wind turbines (Binnemans et al., 2013; DOE, 2011; Graedel et al., 2013). The DOE-identified "short term near-critical" elements cerium and lanthanum are key components of the fluid catalytic cracking (FCC) catalyst used in petroleum refineries to produce gasoline from higher weight crude oil (DOE, 2011). Global supply risks for REE are high because approximately 90% of all REE are currently obtained from a single nation, China (Binnemans et al., 2013).

Waste streams that represent targets for REE recycling include permanent magnets, nickel metal-hydride batteries, and lamp phosphors (Tunsu et al., 2015). Fluorescent lamp wastes in particular present a promising opportunity because of their availability as recycling feedstocks, as they are being generated at increasing volumes throughout the world due to demand for more efficient lighting. Collection systems are already in place for the recovery of some components from fluorescent lamp wastes. Mercury is currently the main driver of the recycling effort because of environmental concerns, but other components (aluminum end caps, plastics, circuit boards, Ni—Cu wire, glass) are also routinely salvaged (DOE, 2011). The phosphor powders that line the bulbs constitute about 2–5% of the total weight of fluorescent lamp waste and are made up of pulverized apatite dust containing REE such as Y, La, Tb, Ce, and Eu (Yang et al., 2013).

To recover REE from solid materials (ores or wastes), physicochemical or biological processes may be employed. Conventional physicochemical methods for REE extraction and separation include dissolution, electrochemical technologies, fractional crystallization, ion exchange, and solvent extraction (Kronholm et al., 2013). These methods are often inefficient when concentrations of the target metals are low. Bioleaching is a hydrometallurgical process that relies on the ability of microorganisms to solubilize and release metal elements from a solid matrix, and it has gained attention in recent years because of its potential for lowering costs and improving environmental sustainability (Brierley and Brierley, 2013). Generally, microorganisms

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facilitate the leaching of metals (including REE) by the production of a mineral or organic acid. The most notable mineral acid-based process is the leaching of copper from ore heaps. This process is accomplished by microorganisms that promote the conversion of insoluble metal sulfides into soluble metal sulfates. Today as much as 18–20% of global copper production uses this technique (Brierley, 2016).

Most REE-containing recycling feedstocks do not contain sulfidic material, and bioleaching by heterotrophic organisms producing organic acids presents an alternative approach. These organisms require organic carbon substrates to support growth and these substrates could be derived from municipal or agricultural wastes for an economical process (Jain and Sharma, 2004). The organic acids would dissolve the solid matrix, and in some cases, enhance metal solubility by complexation (Burgstaller and Schinner, 1993; Gräfe et al., 2011; Jain and Sharma, 2004; Schippers et al., 2014; Uroz et al., 2009). Bioleaching with heterotrophic organisms has been used to recover REE from red mud (a byproduct of aluminum production) and monazite ore. *Penicillium tricolor* RM-10 was able to leach 20–80% of the REE from red mud at a pulp density as high as 10% (Qu and Lian, 2013). Both fungi and bacteria are capable of heterotrophic leaching of monazite, but recovery efficiencies have varied widely. For example, Shin et al. reported 0.1% or less for total REE recovery for a number of heterotrophic bacteria (Shin et al., 2015), while Brisson et al. reported recovery values ranging from 3 to 5% for fungal isolates (Brisson et al., 2015). In contrast, Hassanien et al. reported that *Aspergillus ficuum* and *Pseudomonas aeruginosa* released up to 75% and 64%, respectively, of the REE in monazite (Hassanien et al., 2014).

In this study microbial processes were evaluated for leaching REE from end-of-life waste products, specifically fluorescent lamp wastes and spent petrochemical FCC catalyst. The FCC materials, like the RPP, are considered "low-value" feedstocks, i.e., materials from which REE might not be economically harvested with conventional chemical, electrical, or mechanical methods because of low REE concentrations (Ferella et al., 2016). Microorganisms were enriched and isolated directly from the waste and REE ore materials and three isolates were selected for further study of organic acid production and compared to a known organic acid producing strain. Leaching of REE from RPP and FCC materials using the microbially produced organic acids was compared to leaching using abiotically prepared solutions of gluconic acid, the predominant acid produced by the four microorganisms tested. In addition, the effect of the presence or absence of whole cells during the leaching stage on REE solubilization was examined.

2. Materials and methods

2.1. Substrates for enrichment and leaching

REE ore materials were obtained from the Rare Earth Resources (RER) Bull Hill Mine, located in the Bear Lodge District, north of Sundance, WY. Samples were collected from the main carbonatite dyke zone borehole, 82.9 m below land surface. Spent FCC catalyst (average particle size 80–90 μm; 55–60% Al_2O_3 and 35–40% SiO_2) was obtained from Valero (Houston, TX) and RPP (retorted at 475 °C for 8 h under negative pressure; >90% of particles between 37 and 210 μm; 85–95% apatite mineral and 5–15% ceramic mixture) was provided by AERC Recycling Solutions (Allentown, PA). The REE content of the FCC catalyst and RPP is presented in Table 1; values were determined by acid digestion of the solids using 70% hydrochloric and 30% nitric acid, at 125 °C for 8 h two times, followed by inductively coupled plasma mass spectrometry (ICP-MS) analysis.

Table 1
REE content in FCC catalyst and RPP.

REE	FCC catalyst[1]		RPP[2]	
	Mean (μg/g)	RSD[3] (%)	Mean (μg/g)	RSD (%)
Y	14.0	5.4	50,047.4	2.9
La	13,617.3	2.4	8915.2	6.8
Ce	651.8	6.1	6328.0	6.1
Pr	14.7	2.9	<4.2	1.8
Nd	32.1	1.7	0.5	7.1
Sm	24.2	2.0	<0.2	1.8
Eu	0.7	6.0	3389.2	2.9
Gd	3.8	2.5	104.0	2.3
Tb	0.3	9.8	2575.8	7.9
Ho	1.4	1.8	0.2	15.0
Dy	0.3	1.4	<2.0	1.9
Er	0.7	2.0	<1.8	1.9
Tm	<0.1	3.7	0.9	3.9
Yb	0.4	4.0	0.6	5.1
Lu	0.1	6.0	31.9	6.5
Th	5.7	1.5	<2.6	1.9

[1] FCC, Valero fluid catalytic cracking catalyst (spent).
[2] RPP, AERC retorted phosphor powder.
[3] RSD, relative standard deviation.

2.2. Microorganisms and media

Gluconobacter oxydans strain NRRL B58 was obtained from the Agriculture Research Service, USDA (Peoria, IL). Isolation and organic acid analysis media: yeast-extract peptone glucose medium (YPG; 0.5 g/L yeast extract, 0.5 g/L peptone, 1 g/L glucose) and Pikovskaya phosphate medium (Pikovskaya, 1948). A modified Pikovskaya medium (Pkm) included a replacement of the calcium phosphate with $CaCl_2 \cdot 7H_2O$ (0.3 mM) and KH_2PO_4 (2.7 mM). Pkm was modified to PkmT by including tryptone (10 g/L). Solid media was prepared with agar (15–20 g/L). Enrichment and isolation of microorganisms from the Bull Hill ore used 10% (w/v) sediment slurry in sterile phosphate buffered saline that was diluted and plated on YPG or Pikovskaya agar and incubated at 30 °C for ten days. For RPP, 0.5 g of material was suspended in 50 mL Pkm prior to incubation and plating on Pikovskaya agar for isolation. Isolates growing on Pikovskaya agar plates were evaluated for calcium phosphate clearing zones (>3–5 mm beyond the edge of the colony).

2.3. Molecular DNA techniques for phylogeny determination

Genomic DNA (gDNA) was extracted from the selected isolates using an UltraClean Microbial DNA Isolation kit (Mo Bio, Carlsbad, CA). Bacterial 16S ribosomal RNA (rRNA) genes were amplified by polymerase chain reaction (PCR) using <1 ng gDNA, TaqPlus Precision polymerase (Agilent Technologies, Santa Clara, CA), and primers 8F and 1492R; the fungal 18S rRNA gene was amplified using primer pairs F566 with F1200 and nu-SSU-0817 with nu-SSU-1536 (Borneman and Hartin, 2000; Hadziavdic et al., 2014; Reed et al., 2002). PCR products were purified with a QIAquick PCR Purification kit (QIAGEN) and sequenced (Pocatello, ID; www.mrcf.isu.edu). A consensus nucleic acid sequence was generated for each isolate and aligned pairwise, using the National Center for Biotechnology Information (NCBI) BLASTN tool to identify the closest sequence matches (Morgulis et al., 2008; Zhang et al., 2000). Gene sequences were submitted to GenBank (Accession no. KP216500, KP216504, KP216499).

2.4. Growth and organic acid production

Microbial isolates were grown overnight in Pkm medium at 30 °C with shaking (180 rpm), and sub-cultured to 50 mL Pkm or PkmT medium in a 250 mL flask and incubated with shaking at 150 rpm for up to four days. PkmT medium was included based on preliminary data suggesting that tryptone enhanced growth. Cultures in Pkm were incubated at 20, 30, or 40 °C to test the effect of growth temperature; cultures in PkmT were grown only at 20 °C. The bacterial subcultures were inoculated at 0.5×10^7 to 2×10^7 cells/mL; initial cell numbers were determined by acridine orange direct count (Ghiorse and Balkwill, 1983). For the fungal isolate A1, a 1.5 mL two day old culture (6.2 ± 0.8 mg dry weight) was used as inoculum. All growth experiments were