



Continuous biological sulfate reduction from phosphogypsum waste leachate



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ABSTRACT

This work explores the possibility to utilize biological sulfate reduction in the treatment of phosphogypsum leachate, with a simultaneous removal of sulfate and phosphorus in continuous flow bioreactors. An efficient sulfate reduction was achieved and proof of elemental removal was acquired. The method described in this work is suggested to be applied as a passive type of installment with environmental pollution control as the primary target. In addition to sulfate reduction, rare earth elements (REE) were monitored during the process, as these valuable elements are commonly found in phosphogypsum waste.

1. Introduction

Phosphorus is a vital element for modern society, due to its wide usage as a fertilizer. It is mainly obtained from mining phosphorus ore deposits, where it occurs as apatite minerals, like fluorapatite (Ca₅(PO₄)₃F). (Cooper et al., 2011) Typical process for recovering phosphorus from these ores is sulfuric acid leaching, which results in the production of phosphoric acid, but also the generation of solid phosphogypsum (PG) by-product. Even though the sulfuric acid process is economic, it generates large quantities of waste, illustrated by the global 100–280 Mt. production of PG annually (Reijnders, 2007). Approximately five tons of PG is generated per ton of phosphoric acid produced (Tayibi et al., 2009). This waste is being mainly stockpiled in the vicinity of plants (Reijnders, 2007; Grain, 2011), with a recycling rate of only 15% (Tayibi et al., 2009).

By nature, PG is an acidic by-product and consists mainly of different forms of calcium sulfate. However, it contains also impurities like fluoride, phosphoric acid, trace metals (Cr, Cu, Zn and Cd) and radioactive elements, as well as rare earth elements (REE) (Habashi, 1985). PG is considered a potentially valuable source of REE, because in the sulfuric acid process 70–85% of REE contained in the original feed ends up to PG by-product (Preston et al., 1996). The REE in PG may be present in isomorphous substitution with calcium ions (Ca²⁺) (Kim et al., 2016), and it can also be detected on the surface of gypsum (Walawalkar et al., 2016).

As PG is usually stored in outdoor piles, there is a possibility that

several substances, including sulfate, residual phosphorus and trace elements, as well as acidity can be released to the environment by exposure to rain and generation of seepage waters (Szlauer et al., 1990; Rutherford et al., 1994). Especially sulfate, previously considered as a relatively inert compound, can cause various changes in the aquatic ecosystems, for example oxygen depletion and eutrophication (Kauppi et al., 2013). As sulfate, metals and acidity can be problems with natural PG run-off, an attractive option is to treat all of these in a single process utilizing sulfate-reducing bacteria (SRB). Moreover, residual phosphorus in the seepage waters can, at least partly, be treated by SRB, as bacteria need also some phosphorus for their growth (Madigan et al., 2015).

In biological sulfate reduction, SRB can transform sulfate to sulfide as a part of the natural sulfur cycle (Lens, 2009). The essential prerequisites for this phenomenon are an anaerobic environment and a suitable electron donor and carbon source. In laboratory conditions, a commonly used substrate is lactate (Eq. 1) (Kaksonen et al., 2003; Zhao et al., 2010):



The formed bicarbonate neutralizes acidity of the waste stream and hydrogen sulfide can precipitate a variety of base metals. The fate of REE in such environment is not well understood. According to Gieré (1993), REE₂S₃ has been observed in laboratory experiments, but REE chemistry is also affected by stronger ligands or complexing agents, like fluoride, carbonate, phosphate and sulfate, found from SRB process

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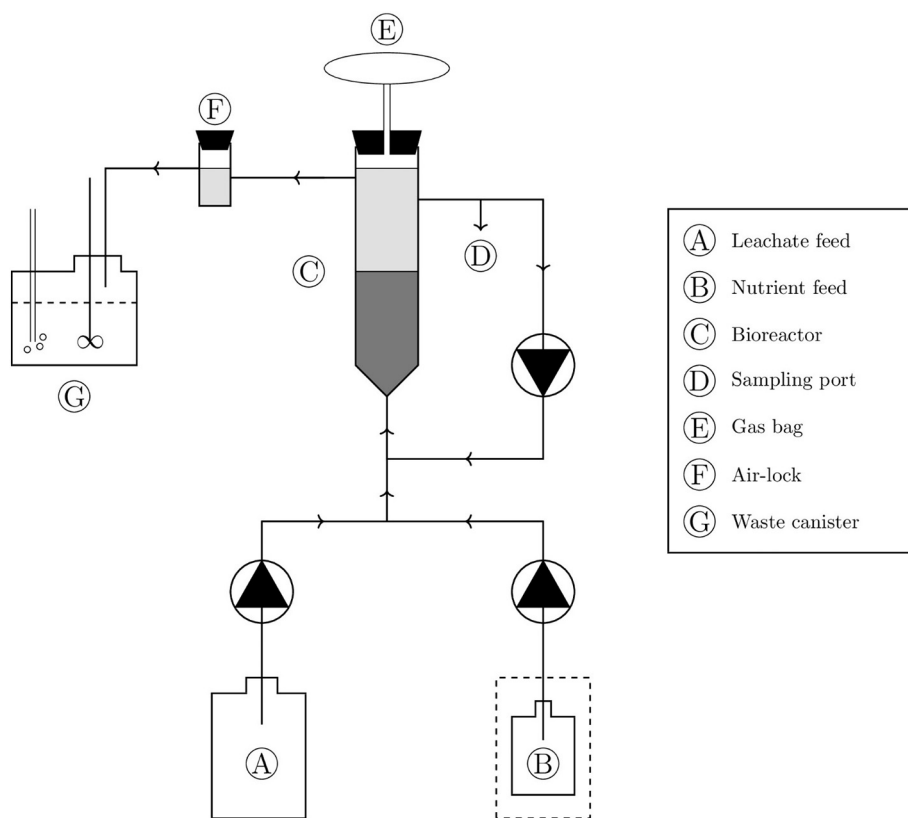


Fig. 1. Process configuration for both bioreactors (for simplicity, only one reactor shown in the diagram).

treating phosphogypsum leachate. Nevertheless, free sulfide is toxic and the excess of it needs to be removed in industrial processes (Moosa and Harrison, 2006). Sulfide can be removed by oxidizing it to elemental sulfur (Eq. 2) or back to sulfate (Eq. 3) (Chen and Morris, 1972):



The preferable pathway would be the one described in Eq. 2, as elemental sulfur has economic value in chemical industry, for example in the manufacturing of fertilizers (Lens, 2009).

Previous studies have shown that waste gypsum can be processed by using SRB. Kaufman et al. (1997) studied an SRB process to treat waste gypsum generated from flue gas desulfurization, aiming to recycle both calcium carbonate and elemental sulfur using a low-cost substrate. Both sulfate removal and elemental sulfur recovery were nearly 100% in a continuously operated bioreactor, resulting in an economic possibility to avoid gypsum landfilling. Azabou et al. (2005) have made a wide study of optimal growth conditions of SRB in PG solution. They explored different parameters, including PG content, carbon source and temperature, which were all compared in terms of sulfide production efficiency in batch experiments. Later Azabou et al. proved that these SRB enriched in PG solution can effectively be used in the recovery of zinc from synthetic waste water (Azabou et al., 2007). Wolicka (2008) and Rzczycka et al. (2010) focused on a combined treatment of PG and waste waters from the agricultural industry. Wolicka (2008) studied the utilization of dairy effluents, and while the organic content of the waste stream was nearly fully exhausted, sulfate reduction remained below 50% in batch experiments. Rzczycka et al. (2010) used pig manure in their batch experiments, and obtained quite the opposite results, with sulfate reduction up to 98% but the organics removal being < 55%.

REE recovery from PG by utilizing SRB is a much less studied topic. An early result of Dudeny and Sbai (1993) indicated that REE can be liberated from PG by subjecting the aqueous solution received as

leachate from PG to SRB. An ion exchanging stage was applied to remove surplus cations from the leachate, and a 77% recovery of yttrium from PG in the elution phase was achieved. The solution was further led to a fixed bed reactor applying sulfate reducing *Desulfovibrio desulfuricans*, with lactate as substrate. Thus, instead of active chemical treatment adapted to the production pace of the phosphoric acid plant, a passive biochemical approach based on SRB could be an option for the REE recovery from PG. In our recent preliminary study (Mäkinen et al., 2017), we utilized water leaching for PG and treated the produced solution by both batch and continuous column experiments for simultaneous sulfate removal and REE recovery. In particular, batch experiments indicated a tendency to precipitate the dissolved REE, producing a solid fraction containing 13.5% (by wt.) REE. In continuous column experiment, REE concentrations in the solid fraction were much lower, due to the diluting effect of carrier material (anaerobic sludge) in the column. However, the REE recovery yields were still high. Due to the promising results of Mäkinen et al. (2017), the method was patented (Patent WO2015075317A1).

In the present study, a semi-passive water leaching of PG (simulating “rain water” exposure of PG heap, resulting in seepage waters) followed by continuous sulfate-reducing bioreactor treatment was examined. Sulfate reduction was evaluated in a long-term (11 months) experiment and phosphorus and REE were monitored in the process. The obtained solid residues from the experiment were collected and studied for a better understanding of the behavior of REE in such process.

2. Materials and methods

2.1. PG leachate preparation

PG waste was collected from a phosphate mine. The sample was dried in an oven at 50 °C. PG leachate for the bioreactor experiments was prepared by mixing PG waste in ion-exchanged water (10 g/L) for

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