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Research article

Recovery of Al, Cr and V from steel slag by bioleaching: Batch and column experiments

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ABSTRACT

Steel slag is a major by-product of the steel industry and a potential resource of technology critical elements. For this study, a basic oxygen furnace (BOF) steel slag was tested for bacterial leaching and recovery of aluminium (Al), chromium (Cr), and vanadium (V). Mixed acidophilic bacteria were adapted to the steel slag up to 5% (w/v). In the batch tests, Al, Cr, and V were bioleached significantly more from steel slag than in control treatments. No statistical difference was observed arising from the duration of the leaching (3 vs 6 d) in the batch tests. Al and Cr concentrations in the leachate were higher for the smaller particle size of the steel slag (< 75 μm), but no difference was observed for V. In the column tests, no statistical difference was found for pH, Al, Cr and V between the live culture (one-step bioleaching) and the supernatant (two-step bioleaching). The results show that the culture supernatant can be effectively used in an upscaled industrial application for metal recovery. If bioleaching is used in the 170–250 million tonnes of steel slag produced per year globally, significant recoveries of metals (100% of Al, 84% of Cr and 8% of V) can be achieved, depending on the slag composition. The removal and recovery percentages of metals from the leachate with Amberlite®IRA-400 are relatively modest (< 67% and < 5%, respectively), due to the high concentration of competing ions (SO_4^{2-}, PO_4^{3-}) in the culture medium. Other ion exchange resins can be better suited for the leachate or methods such as selective precipitation could improve the performance of the resin. Further research is needed to minimise interference and maximise metal recovery.

1. Introduction

In 2016, the global steel production was 1360 million tonnes (WSA, 2017), generating around 170 to 250 million tonnes of steel slag as a major by-product (Gomes et al., 2016b; USGS, 2017a). Recycling of this slag as construction materials has long been a research focus and an established afteruse, with up to 70% of slag in Europe reused (48% in road construction, 10% in metallurgical processes, 6% in cement production, 3% in hydraulic engineering and 3% as fertilizer, in 2010) (Euroslag, 2017; Fakhri and Ahmadi, 2017; Gajda et al., 2017; Garg and Singh, 2016; Gutierrez et al., 2016; Zhao et al., 2017). Although metal recovery from wastes is becoming a key process in the context of a circular economy (Haas et al., 2015; Hagelüken et al., 2016), metal recovery from steel slag has been largely confined to bench scale studies thus far (Gomes et al., 2017). Also, several obstacles can limit full implementation, such as regulatory constraints (e.g. definition of waste, environmental permits), ownership (slag belongs to the aggregate company, but the leachate is the responsibility of the producer), and liabilities arising from past action and owners (Deutz et al., 2017). Without a sustainable technology for large scale processing of slags, stockpiling in heaps and tailings is the usual management practice, potentially causing environmental problems due to dust generation and accidental leakage of alkaline drainage (pH > 12) (Gomes et al., 2016b; Kaksonen et al., 2017).

Bioleaching is a mature hydrometallurgical technology, which relies on microorganisms to solubilise metals primarily through the production of a mineral or organic acid, and it is widely employed commercially for processing pyrite-rich, low-grade copper sulphide ores (Reed et al., 2016; Rodrigues et al., 2016). The approach benefits from low energy input, low capital cost and it requires only unskilled labour, and this has underpinned increasing research focus onto bioleaching in recent years (Funari et al., 2017; Rastegar et al., 2015; Reed et al., 2016). Bioleaching has only recently been investigated as a potential route for the valorisation of alkaline wastes, as a pre-treatment to mineral

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carbonation or for removal of toxic metals which facilitates further reuse or valorisation (Chiang et al., 2013). Steel slag can be a valuable secondary resource if processed with low energy consumption and minimal environmental impacts for secured supply of metals (Hocheng et al., 2014).

There are few studies on metal bioleaching from steel slag. Pure cultures such as *Acidithiobacillus ferrooxidans* were tested in blast furnace sludge and flue dust (Banerjee, 2007). Bioleaching of smelter slag was tested using a mixed culture enriched from a sulphide ore mine site, which contained *Acidithiobacillus* spp. and *Leptospirillum* spp. for the recovery of Zn and Fe (Vestola et al., 2010). In all these studies, one step bioleaching was performed where the microorganism is inoculated together with the slag in the medium and microbial growth, and metal leaching co-occur (Pandey and Natarajan, 2015). In two-step bioleaching (or spent medium leaching), after the maximum growth of the microorganism and consequent maximum production of metabolites occurred, the suspension is filtered, and only the filtrate is used for leaching (Pandey and Natarajan, 2015). Culture supernatants of *Acidithiobacillus thiooxidans*, *Acidithiobacillus ferrooxidans*, and *Aspergillus niger* were used with electric arc furnace (EAF) slag for two-step bioleaching (Hocheng et al., 2014). *Acidithiobacillus thiooxidans*, *Pseudomonas putida* and *Aspergillus niger* were tested with roasted Linz-Donawitz converter slag for vanadium recovery (Mirazimi et al., 2015) in one and two-step bioleaching. However, further research is needed to determine: which culture or mixed cultures enhance steel slag bioleaching; if one-step or two-step bioleaching is more effective; the optimal time of exposure; and how to recover metals from the bioleachate.

This study investigates steel slag bioleaching for the removal of Al, Cr and V in batch and column tests using a mixed culture of acidophilic bacteria and its cell-free supernatant applied for the first time to steel slag, under different experimental configurations. Recovery performances of those metals from the bioleachates were tested using an anion exchange resin to determine the value chain potential and establish a testing ground for a large-scale rollout. The main objectives were to i) determine the bioleaching yields in column and batch experiments; ii) assess if the particle size affected the steel slag bioleaching; iii) assess if the duration of the experiments influenced bioleaching; and iv) evaluate recovery of metals from the bioleachate using a commercial ion exchange resin.

2. Materials and methods

2.1. Materials and chemicals

Basic oxygen furnace (BOF) steel slag was collected from Yarborough, Scunthorpe, UK (53°35′07.3″N 0°35′35.5″W) in December 2016. The primary sample was ground (fly press and vibrating mill Siebtechnik) and sieved into three different fractions: < 75 μm, < 2 mm, and 4 < size > 10 mm (typically used for pipe bedding). The first two fractions were used in the batch tests, and the third for the column tests to investigate a granulometry that would not require as much mechanical crushing before leaching.

The bacteria mixed culture was cultivated in a modified 9 K medium (Funari et al., 2017; Silverman and Lundgren, 1959) containing $(NH_4)_2SO_4$ 3.0 g L^{-1}, K_2HPO_4 0.5 g L^{-1}, $MgSO_4{\cdot}7H_2O$ 0.5 g L^{-1}, KCl 0.1 g L^{-1}, $Ca(NO_3)_2$ 0.01 g L^{-1}, $FeSO_4{\cdot}7H_2O$ 22.5 g L^{-1} and 10.0 g L^{-1} S^0. The modified 9 K medium was adjusted to pH 2.0 with concentrated H_2SO_4. All reagents used were of analytical grade.

The ion exchange resin used for assessing the metal recovery was Amberlite® IRA-400 (Sigma-Aldrich), which is a strong base anion exchange resin with quaternary ammonium functional groups (–N + R3) in a polystyrene matrix, and particle sizes of 600–750 μm. Before use, the resin was converted to the hydroxide form according to Gomes et al. (2017).

2.2. Adaptation of the bacteria culture

The mixed acidophilic culture used for the bioleaching experiments was obtained by combining several samples from overflows and ponds of the Libiola Fe-Cu mine area (Ligurian Apennines, Italy), collected at the sediment-water interface. The pH of the original liquid samples varied between 1 and 3 and the samples contained red-brown iron(III) precipitates (not analysed in this study) (Dinelli et al., 2001). *Acidithiobacillus thiooxidans* and *Acidithiobacillus ferrooxidans* are the dominant strains in the natural culture. A preliminary terminal restriction enzyme fragment length polymorphism (T-RFLP) analysis report is presented in Table S1 (Supplementary Information). Initial conditioning of the original culture, which comprised a turbid suspension of water, minerals, and biomass, was performed in flasks containing 90% (v/v) modified 9 K medium on a shaker incubator (Infors HT Multitron Standard). The pH was maintained below 2.5 using concentrated H_2SO_4, as required. The total volume of H_2SO_4 added in the three rounds of adaptation was 330 μL per flask. The culture was incubated at 150 rpm and 30 °C. To enhance the cell activity, the culture was renewed every 15 days by inoculating 10% (v/v) of former cultivation and 90% (v/v) of the modified 9 K medium.

The original acidophilic culture was adapted to tolerate the presence of steel slag, and the adaptation phase was conducted in 250 mL Erlenmeyer flasks containing 90 mL of the modified 9 K medium. Flasks were inoculated with the acidophilic culture (10% v/v) followed by the addition of the steel slag. Before the adaptation, the steel slag was autoclaved for 30 min at 135 °C, assuring that no other microorganisms than those inoculated were present. The pH was adjusted to 2.0 with concentrated H_2SO_4, and flasks were incubated on the same incubator (150 rpm, 30 °C). Growth of bacteria was monitored by measuring pH and redox potential. If a spontaneous decrease in pH was observed during 15 days due to the growth and activity of the sulphur oxidising acid-generating bacteria, a new modified 9 K medium with an increased amount of steel slag was prepared and inoculated with the previous solution (10% v/v) of the adaptation phase. As part of the adaptation process, the quantities of slag were increased three times (1, 2, and 5%) of L/S ratio. The culture successfully tolerated the addition of up to 5% steel slag, and that adapted inoculum was used for the experiments.

2.3. Batch experiments

The leaching experiments (one-step bioleaching) were carried out in triplicate in 500 mL Erlenmeyer flasks with 1.0 g of steel slag (< 75 μm and < 2 mm fractions), with 90 mL of culture medium and 10 mL of the adapted inoculum. The flasks were shaken on an incubator shaker (Infors HT Multitron Standard) at 150 rpm at 30 °C for 3 and 6 d, as maximum metal extraction was achieved in six days by *At. thiooxidans* culture supernatant (Hocheng et al., 2014). Then, 10 mL of the mixture was sampled for further analysis. Control tests without inocula (mixed acidophilic culture) were performed under the same conditions.

2.4. Column experiments

Column experiments were conducted in a 1.8 cm diameter × 35 cm height acrylic (Plexiglas) tube in which 100 g of steel slag (4 mm < size > 10 mm) was packed. The experiments lasted 22 days. The column experiments were carried out at controlled temperature (28 ± 1 °C). All columns were fed from the top from a 2 L flask at a flow rate of 5 mL min^{-1}, which was controlled by a peristaltic pump (Watson-Marlow, Falmouth, UK) and the feeding solution was then recirculated (closed-loop tests). We ran a set of column experiments to assess the yields between one-step bioleaching and two-step bioleaching. In experiment A (two-step bioleaching), the leaching solution was 1 L of the supernatant of the cultures after filter sterilisation (vacuum filtration, cellulose nitrate filters Sartorius Stedim Biotech 0.22 μm). In experiment B (one-step bioleaching), the leaching solution