



Sequential biological process for molybdenum extraction from hydrodesulphurization spent catalyst



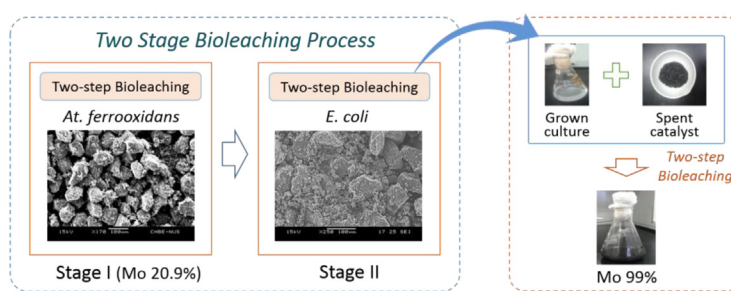
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HIGHLIGHTS

- Bioleaching using *Escherichia coli* is reported for the first time.
- A two-stage bioleaching process outlined for higher Mo recovery.
- 1st stage yield 89% Ni and 21% Mo extraction.
- Two-stage bioleaching yielded 99% extraction of remaining Mo.
- Product layer diffusion was rate determining step in Mo leaching.

GRAPHICAL ABSTRACT



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ABSTRACT

Spent catalyst bioleaching with *Acidithiobacillus ferrooxidans* has been widely studied and low Mo leaching has often been reported. This work describes an enhanced extraction of Mo via a two stage sequential process for the bioleaching of hydrodesulphurization spent catalyst containing Molybdenum, Nickel and, Aluminium. In the first stage, two-step bioleaching was performed using *Acidithiobacillus ferrooxidans*, and achieved 89.4% Ni, 20.9% Mo and 12.7% Al extraction in 15 days. To increase Mo extraction, the bioleached catalyst was subjected to a second stage bioleaching using *Escherichia coli*, during which 99% of the remaining Mo was extracted in 25 days. This sequential bioleaching strategy selectively extracted Ni in the first stage and Mo in the second stage, and is a more environmentally friendly alternative to sequential chemical leaching with alkaline reagents for improved Mo extraction. Kinetic modelling to establish the rate determining step in both stages of bioleaching showed that in the first stage, Mo extraction was chemical reaction controlled whereas in the subsequent stage, product layer diffusion model provided the best fit.

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1. Introduction

With the rapidly growing demand for heavy metals such as Ni and Mo, secondary resources including spent catalyst generated by refineries have become increasingly important. Catalyst used for

hydro-treating applications usually contain nickel or cobalt and molybdenum or vanadium on an alumina base. The catalyst become deactivated by several mechanisms such as coke formation, metal deposition and active phase sintering (Marafi and Stanislaus, 2003; Vogelaar et al., 2010). Depending on the type of feed (such as residue, middle distillates, and vacuum gas oil), the catalyst losses activity over a period of time and is deemed spent. The importance of removal or recovery of heavy metals from spent catalyst is not only due the need for resource recovery and but is

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also because of stringent environmental regulations. Spent catalyst contains heavy metals and is considered a hazardous waste which requires treatment before disposal. Bioleaching may be able to effect metal extraction via biogenically produced metabolites and thus provides a green alternative to chemical leaching processes. Spent catalyst bioleaching have been examined with fungi such as *Aspergillus niger* and *Penicillium simplicissimum* (Amiri et al., 2011; Aung and Ting, 2005; Santhiya and Ting, 2005). Leaching with fungal microorganisms is mainly based on acidolysis and complexation of metals by the excreted metabolites such as organic acids and amino acids.

Acidophilic bacteria (such as *Acidithiobacillus thiooxidans* (*At. thiooxidans*) and *Acidithiobacillus ferrooxidans* (*At. ferrooxidans*)) are also used for spent catalyst bioleaching (Mishra and Rhee, 2010; Pradhan et al., 2013; Srichandan et al., 2014). Proton (H^+) and Fe^{3+} produced by bacterial oxidation of sulphur and Fe^{2+} respectively, play a significant role in metal extraction from the solid substrate. The ineffective extraction of Mo (from MoS_2) under acidic conditions is due to the molecular orbital structure of the metal sulphide which is resistant to proton attack (Sand et al., 2001). For other metal sulphides (except FeS_2 , MoS_2 , and WS_2), in addition to an oxidants such as iron (III) ions, an additional attack is performed by protons which remove electrons from the valence band, causing a cleavage of the bonds between the metal and the sulphur moiety of the metal sulphide. Consequently, these metal sulphides are relatively soluble in acid (Beolchini et al., 2010; Sand et al., 2001; Schippers and Sand, 1999). Iron (II)-oxidizing bacteria (e.g. *At. ferrooxidans*) catalyse the recycling of iron (III) ions in acidic solutions. Higher extraction of Ni as compared to Mo during spent catalyst bioleaching by acidophiles is also due to this phenomena.

In a study, two-step bioleaching of spent catalyst at a pulp density of 1.5% using *At. thiooxidans* resulted in only 17.4% Mo leached as compared to 88.2% Ni (Mishra et al., 2008). An examination of the reaction kinetics showed that bioleaching rate of the metals was best described by the product layer diffusion control model. Similarly, with *At. ferrooxidans*, high Ni leaching of about 90–95% was observed while Mo leaching was low (Pradhan et al., 2013). The lower Mo recovery has been attributed to the insolubility of the metal under acidic conditions and subsequent precipitation as molybdenum trioxide. Another study attributed the lower leaching of Mo (as compared to Ni and V) to the refractory nature of MoS_2 and the presence of elemental sulphur layer on catalyst surface (Pradhan et al., 2010).

On examining the toxic effect of Mo^{6+} , Ni^{2+} and V^{4+} on the ferrous oxidising ability of *At. ferrooxidans* (Pradhan et al., 2009), Mo^{6+} was found to be most toxic and as expected, the lowest extraction of Mo^{6+} was observed. Adaptation of the bacteria led to around 50% Mo leaching, a result still significantly lower than the more than 90% leaching of Ni and V (Kim et al., 2010).

Various strategies have been adopted for improved extraction of metal in spent catalyst bioleaching and few studies have reported Mo leaching comparable to Ni using acidophiles. Efforts to improve Mo extraction include pretreatment of spent catalyst, microbial adaptation and use of extreme thermophiles or fungal strains (Amiri et al., 2011; Bharadwaj and Ting, 2013; Santhiya and Ting, 2006). In another approach, an additional chemical leaching step was introduced (Pradhan et al., 2013). After bioleaching with *At. ferrooxidans*, post treatment with ammonium carbonate resulted in around 99% of Mo recovery as compared with 53% with bioleaching alone. Although treatment with sulfuric acid following bioleaching have been attempted, higher recovery was obtained with ammonium carbonate which provided alkaline conditions.

Recently, two-stage bioleaching (i.e. bioleaching-bioleaching) of spent catalyst was reported and compared with bioleaching followed by chemical leaching in the second stage (Srichandan et al.,

2014). In the two-stage bioleaching, the same bacteria (*At. ferrooxidans* or *At. thiooxidans*) was used in both stages and was found to be less effective as compared to a subsequent alkaline (chemical) leaching. The higher Mo leaching was due to higher solubility at alkaline pH since Mo exists as soluble MoO_4^{2-} at alkaline pH, as compared to insoluble $MoO_3 \cdot H_2O$ under acidic condition (Srichandan et al., 2014). Different fractions representing various chemical forms of metal and require dissimilar conditions for complete extraction (Pathak et al., 2014). Thus, providing alkaline conditions subsequent to acidic bioleaching enhances the dissolution of both reducible and oxidizable fractions of spent catalyst. Since Mo was present both as oxide and sulphide, it followed a dissolution pattern different from sulphide oxidation (Beolchini et al., 2009; Kim et al., 2010). Thus, a reducing agent was required for complete dissolution and may be added externally or produced during bacterial fermentation. *Escherichia coli* (*E. coli*) provides reducing conditions which may enhance Mo extraction. Motivated by this, we proposed a two-stage bioleaching process to improve Mo extraction, using *E. coli* in the second stage. Thus, initial bioleaching with *At. ferrooxidans* dissolves sulfides and additional step may assist in extraction of the remaining metals.

2. Materials and method

2.1. Materials

Spent catalyst (DC-2534) used for bioleaching experiments was kindly provided by Criterion Catalyst and Technologies, and Shell Eastern Petroleum (Pte) Ltd, Singapore. The spent catalyst was dry screened through sieves, and catalyst of 75–100 μm size range was used.

Acidithiobacillus ferrooxidans (*At. ferrooxidans*) was used for first stage bioleaching and was kindly provided by Prof. Natarajan (Indian Institute of Science, Bangalore). Actively grown culture of *At. ferrooxidans* was inoculated (15% v/v) in a media containing $(NH_4)_2SO_4$ 2.00 g/l, K_2HPO_4 0.50 g/l, $MgSO_4 \cdot 7H_2O$ 0.50 g/l, KCl 0.10 g/l, $Ca(NO_3)_2$ 0.10 g/l and $FeSO_4 \cdot 7H_2O$ 8.00 g/l. Initial pH was adjusted to 2.0 using H_2SO_4 . Batch cultures were grown in 250 ml conical flasks containing 100 ml of media at 30 °C and 150 rpm.

Escherichia coli DH5a (ATCC[®] 53868™) was used for the second stage of bioleaching. Actively grown culture of *E. coli* was inoculated (2% v/v) in LB Miller broth. Batch cultures were grown in 250 ml conical flasks containing 100 ml of media at 37 °C and 150 rpm.

2.2. Methods

Scanning Electron Microscopy (SEM) (Joel JSM-5610) was used to observe the surface morphology of the spent catalyst. In the first stage, two-step bioleaching of spent catalyst (at 1% pulp density, 75–100 μm) was conducted using *At. ferrooxidans*. The catalyst was autoclaved and added after the culture had grown for 7 days. Experiments were conducted with 100 ml of media (initial pH 2.0) in 250 ml conical flasks which were maintained at a constant temperature and agitation in an orbital shaker incubator (YIH DER, model LM-570R). At pre-determined time intervals, 2 ml of samples were taken for pH (Thermo scientific ORION 720A) and metal analyses. After bioleaching, the catalyst was collected and air dried (60 °C) before the subsequent second stage two-step bioleaching using *E. coli* (also at 1% pulp density). The bioleached catalyst was added to the flasks after 24 h of growth ($\approx 4-5 \times 10^9$ CFU/ml). All the experiments were conducted in duplicates. The spent and bioleached catalyst were digested following the protocol in US EPA SW 846 Method 3050 B. Toxicity Characteristic Leaching Procedure (TCLP) test was conducted following the protocol in US EPA SW 846 Method 1311. The concentration of heavy metals (Ni, Mo and Al)

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