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Sequential leaching of metals from spent refinery catalyst in bioleaching–bioleaching and bioleaching–chemical leaching reactor: Comparative study

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ABSTRACT

The effect of sequential leaching such as bioleaching followed by bioleaching and bioleaching followed by chemical leaching is aimed at enhancing metal (Mo, Ni, V and Al) dissolution from a differently pretreated (acetone washed/decoked) spent catalyst. The X-ray photoelectron spectroscopy characterization of spent catalyst samples suggested the presence of metals in their oxide and sulfide forms. Bioleaching followed by bioleaching with either *Acidithiobacillus thiooxidans* (Ni-100%, Al-55%, Mo-81% and V-100%) or *Acidithiobacillus ferrooxidans* (Ni-94%, Al-55%, Mo-77% and V-99%) significantly enhanced removal of Al, Ni, and V from acetone washed (AS) spent catalyst compared to decoked spent catalyst (RS). In contrast, bioleaching using either *A. thiooxidans* or *A. ferrooxidans* followed by alkali leaching remarkably enhanced removal of Mo from both AS and RS, although higher yields were achieved using AS. Bioleaching using *A. thiooxidans* followed by alkaline leaching is an optimum strategy yielding a maximum of 96% Mo in 125 h from AS. A field emission scanning electron microscopic study revealed only minor stretches of Mo in the treated AS.

1. Introduction

The petroleum refinery industry use huge quantities of solid catalysts to convert crude oil into useful products. Treating crude oil via reforming, hydrocracking, hydrotreating, catalytic cracking, and alkylation produces valuable oil products such as fuel oil, gas oil, kerosene, jet fuel, gasoline, and naphtha (Furimsky, 1996). Catalyst activity decreases with time and, hence, they are reactivated, reused, and finally disposed of as waste materials. These waste materials are referred as "spent catalyst", which contain different metals such as Al, Co, Fe, Mo, Ni and V. The metals in the spent catalyst are present in the form of metal ions, metal oxides, and metal sulfides (Marafi and Stanislaus, 2003). Spent catalyst has been categorized as hazardous by the USEPA and cannot be disposed of without treatment. Various hydrometallurgical processes have been used to remove metal from spent catalyst. The hydrometallurgical processes have used high concentration of acid (8 M H_2SO_4) and alkali (4 M NaOH) for removing metals from spent catalyst (Ognyanova et al., 2009; Park et al., 2007). Although, hydrometallurgical processes have shown reasonable metals extraction efficiencies, the use of high strength acids and alkali, secondary pollution and expensive downstream processing has restricted their usage on a larger scale. Different pyrometallurgical techniques such as smelting, calcination, anhydrous chlorination have also been employed to recover metals from spent catalyst (Kar et al., 2005). However, pyrometallurgical processes suffer with the use of high energy consumption and emit toxic gases into the atmosphere. Therefore, the use of relatively benign bio-hydrometallurgical processes for recovery of metals from spent petroleum catalysts is gaining attention.

Bioleaching has emerged as an efficient, eco-friendly and cost effective process to recover metals form spent catalyst. Bioleaching is based on the metabolic activity of various chemoautotrophic bacteria (*Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans)* and heterotrophic fungi *(Aspergilus niger)*. Various bioleaching studies have used *A. ferrooxidans* and *A. thiooxidans* to recover metals from spent catalyst (Gholami et al., 2011; Pradhan et al., 2010). The effects of various process parameters such as substrate concentration, pulp density, particle size, and pH on bioleaching have been examined (Kim et al., 2010). The efficacy of bioleaching has also been examined using different types of spent catalysts such as vanadium-rich spent catalyst and spent nickel oxide catalyst (Mishra et al., 2007; Mulak et al., 2005). Treatment of spent catalyst prior to bioleaching is more efficacious than untreated catalyst in terms of metal leaching (Bharadwaj and Ting, 2013).

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Although these studies suggest the potential of bioleaching for metal recovery from petroleum refinery spent catalysts, the longer reaction time (up to 70 days) is still a major hindrance to apply the process on a large scale (Santhiya and Ting, 2005). Moreover, single stage bioleaching alone is insufficient to remove all Mo present in spent catalyst (Mishra et al., 2009; Pradhan et al., 2010) due to either the limited solubility of Mo in a weekly acidic solution or refractory nature of MoS_2 or formation of product layer on the Mo matrix or due to combined effect of all. Therefore, a second treatment step is required to remove the remaining Mo present in the bioleach residue. Our previous study suggested that a sequential reactor employing bioleaching followed by alkaline leaching significantly improves Mo leaching yields from spent catalyst (Pradhan et al., 2013). However, that study was conducted using only *A. ferrooxidans* as a leaching microorganism in the first stage and acetone washed spent catalyst as a feed material.

Besides *A. ferrooxidans*, another acidophile, *A. thiooxidans*, is also capable of leaching metals from spent refinery catalyst using sulfur as an energy source. The use of *A. thiooxidans* during bioleaching can be advantageous due to the comparatively low cost of sulfur. Furthermore, the type of pretreatment (decoking/roasting) of spent catalyst also significantly impacts efficiency of the bioleaching process (Bharadwaj and Ting, 2013) and the efficacy of the process need to be tested using differently pretreated spent catalyst (decoked/organic washed spent catalyst). Moreover, the efficiency of bioleaching using either *A. ferrooxidans* or *A. thiooxidans* in the second stage has not been documented or implemented in previous studies. Therefore, more in-depth sequential reactor studies using differently pretreated spent catalysts and microorganisms are required to develop an efficient and economical process for leaching metals from spent refinery catalyst.

The aim of this study was to develop a robust sequential bioleaching process for enhanced Mo solubilization along with other metals over a shorter duration. Different sequential strategies such as bioleaching followed by bioleaching and bioleaching followed by alkali leaching were evaluated using different pretreated spent catalyst samples and by using different leaching microorganisms. In the first stage, two types of pretreated spent catalysts (acetone washed and decoked) were separately bioleached using sulfur (*A. thiooxidans*) and both sulfur and iron-oxidizing (*A. ferrooxidans*) microorganisms. The bioleached residues obtained from the first stage were further subjected to second stage bioleaching as well as alkali leaching separately to identify the optimum strategy in terms of Mo recovery along with other metals.

2. Materials and methods

2.1. Spent petroleum catalyst pretreatment and characterization

The spent catalyst used was received in bulk from a petroleum refinery company located in South Korea. The raw spent catalyst (SR) was coated with oily matter and was subjected to acetone washing in a Soxhlet apparatus followed by drying in a hot air oven. Similarly, another SR was decoked in a muffle furnace for 5 h at 500 °C in the presence of atmospheric oxygen. The dried acetone washed (AS) and decoked (RS) spent catalysts were ground separately using a vibrating cup mill (Fritsch, Darmstadt, Germany). Particle size distribution was determined by using Malvern Laser Mastersizer. The particle size distribution for RS was 0.025–125 μm. The particle size distribution for AS was 1–200 μm. pH was measured using an Orion portable pH meter, whereas redox potential (ORP) was measured using a platinum electrode with an Ag/AgCl reference electrode. Ferrous (Fe^{2+}) ion was estimated using the 1,10-phenethroline-spectrophotometry method at 510 nm. The sulfur and carbon content was analyzed with a LECO CS-600 analyzer. The surface topography of SR, AS, RS, and the final leach residues was examined using field emission scanning electron microscopy (FESEM; model Magellan 400). Metal content (Ni, Al, Mo, and V) of the spent catalyst was determined by induced couple plasma optical emission spectroscopy (PerkinElmer Optima 8000; Waltham, MA, USA). The chemical and valence states of the metal sulfides and oxides in the spent catalyst samples were determined using X-ray photoelectron spectroscopy (XPS; Thermo Scientific model-Sigma probe; Indianapolis, IN, USA) at a beam voltage of 15 kV and a beam current of 6.7 mA. Monochromatic AlKα (1486.7 eV) X-ray radiation was allowed to fall at 30° on a powdered sample placed on carbon tape. The emitted electrons from the sample were detected by an analyzer placed at an angle of 40°.

2.2. Microorganism and growth conditions

Pure strains of *A. ferrooxidans* and *A. thiooxidans* were obtained from the Korea Research Institute of Bioscience and Biotechnology Culture Collection Center. *A. ferrooxidans* was grown in IEM medium (Blight and Ralph, 2004) and provided with 20 g L^{-1} of $FeSO_4.7H_2O$. The final pH of the medium was adjusted to 1.68 ± 0.05 using concentrated H_2SO_4. *A. ferrooxidans* was allowed to grow in the nutrient medium leading to complete oxidation of ferrous iron. After complete oxidation of ferrous to ferric ions, the growth medium was passed through a 0.45 μm membrane filter to separate the cells. After filtration, the cells were inoculated in a batch reactor for further growth.

A. thiooxidans was grown in 0 K (9 K medium without 9 g of Fe^{2+}) medium composed of $(NH_4)_2SO_4$ (3 g), KCl (0.1 g), K_2HPO_4 (0.5 g), $MgSO_4.7H_2O$ (0.5 g), $Ca(NO_3)_2$ (0.01 g) dissolved in distilled water at final volume of 1 L. Final pH was adjusted to 3.3 ± 0.05 using concentrated H_2SO_4. 1% (w/v) of S^0 was added as an energy source to this medium. Due to the oxidation of S^0 into sulfuric acid, pH of the growth medium was decreased to 1.4. The cells during this log growth phase were separated using a 0.45 μm membrane filter and inoculated for further growth.

2.3. First stage bioleaching

Experiments were carried out in stirred tank batch reactors (2.5 L). All experiments were performed under controlled environmental conditions: initial pH, 1.4 ± 0.05; stirring speed, 250 rpm; temp, 35 °C; working volume, 1 L. Continuous air was supplied to all reactors at a flow rate of 1 LPM to ensure homogenous mixing of the bioleaching pulp. A schematic representation of different strategies employed is provided in the graphical abstract. Prior to the adding the spent catalyst, *A. ferrooxidans* cells were suspended in fresh IEM medium, supplemented with 1% S^0 (w/v) and 4 g L^{-1} Fe^{2+} at pH 1.68. After addition of *A. ferrooxidans*, the planktonic cell count in the reactors was found to be 9×10^7 mL^{-1}. *A. ferrooxidans* is capable of oxidizing both S^0 and Fe^{2+} and generate sulfuric acid and ferric iron as lixiviants during bioleaching. Therefore, to utilize the potential of these lixiviants (sulfuric acid and ferric iron), both S^0 and Fe^{2+} were provided as energy sources during bioleaching. When all Fe^{2+} oxidized to Fe^{3+} and the pH of the medium decreased to 1.4 as a result of oxidation of sulfur to sulfuric acid, AS and RS were (1% w/v) added to separate reactors.

Similarly, in the case of bioleaching with *A. thiooxidans*, bacteria were suspended in 0 K medium supplemented with 1% (w/v) S^0 at pH 3.3 ± 0.05. After addition of *A. thiooxidans*, the planktonic cell count in these reactors was found to be 3×10^7 mL^{-1}. *A. thiooxidans* can oxidize only S^0 and hence S^0 was provided as a sole energy source for its growth during bioleaching experiments. When the pH of the medium decreased to 1.4, AS and RS (1% w/v) were added to separate reactors. The changes in pH, redox potential and metal solubilization were monitored over time. Two separate control reactors (without cells and sulfur) were also used by adding AS and RS (pH 1.4) under similar operating conditions. The changes in pH, redox potential and metal solubilization were monitored over a period of 120 h, and samples were withdrawn every 20 h. The samples were centrifuged, and the liquid was analyzed for metal content. The leaching yield of the desired element was calculated based on both the elemental content of the feed and the leach liquor.