CHEMICAL ENGINEERING TRANSACTIONS Volume 21, 2010
Editor J. J. Klemeš, H. L. Lam, P. S. Varbanov
 ISBN 978-88-95608-05-1 ISSN 1974-9791
DOI: 10.3303/CET1021248

Comparison of Different Methods in Bioleaching of Tungsten- Rich Spent Hydro-Cracking Catalyst Using Adapted *Penecillum simplicissimum* BBRC-20019

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This study was designed to compare one-step, two-step and spent medium bioleaching of spent catalyst by adapted *Penecillum simplicissimum* in batch cultures. *Penecillum simplicissimum* which was adapted to heavy metal ions Ni, Mo, Fe, and W grew in the presence of up to 5 *%w/v* of spent catalyst in the medium. The main lixiviant in bioleaching was gluconic acid which was produced mainly in present and absence of spent catalyst. A total of 3 *%w/v* spent catalyst generally gave maximum extraction yields in two-step bioleaching process, which the amounts of leached metals were 100 % of W, 100 % of Fe, 92.7 % of Mo, 66.43 % of Ni, and 25 % of Al. The red pigment produced by fungus could also possibly act as an agent in Al leaching.

1. Introduction

Large quantities of catalysts are used in the refining industry for the purification and upgrading of various petroleum streams and residues (Marafi and Stanislaus, 2003). The quantity of spent hydro-processing catalysts discarded as solid wastes in the petroleum refining industries has increased remarkably in recent years due to a steady increase in the processing of heavier feedstock (Marafi and Stanislaus, 2008). Due to their toxic nature, spent hydro-processing catalysts have been branded as hazardous wastes, and the refiners are experiencing pressure from environmental authorities to handle them safely (Marafi and Stanislaus, 2003, 2008; Mishra et al., 2007, 2008; Aung and Ting, 2005; Santhiya and Ting, 2005, 2006). Spent hydro-processing catalysts contain various hazardous components, such as W, Mo, Ni, V, Co, Al, and some organic contaminants (Marafi and Stanislaus, 2008; Santhiya and Ting, 2006). Due to strict environmental regulations and economical conditions, proper recovery of the valuable metals from the catalysts has become essential (Marafi and Stanislaus, 2003, 2008; Mishra et al., 2007, 2008; Khin and Ting, 2005; Santhiya and Ting, 2005, 2006). The bioleaching of industrial waste materials such as municipal solid waste incineration fly ash, spent catalyst and electronic scrap of computer, for detoxifying these materials has also been considered more economical and environmentally friendly, as compared to traditional

Please cite this article as: Amiri F., Yaghmaei S., Mousavi S. M., (2010), Comparison of Different Methods in Bioleaching of Tungsten- Rich Spent Hydro-Cracking Catalyst Using Adapted Penecillum simplicissimum BBRC-20019, Chemical Engineering Transactions, 21, 1483-1488 DOI: 10.3303/CET1021248

metals extraction methods with high energy cost and increase in pollution load of environment (Mishra et al., 2007, 2008; Khin and Ting, 2005; Santhiya and Ting, 2005, 2006).

In this investigation, adaptation of *Penecillum simplicissimum* BBRC-20019 with different heavy metals present in the spent hydro-cracking catalyst, and comparing one-step, two-step and spent medium bioleaching of spent catalyst by adapted fungus was examined in batch cultures.

2. Materials and methods

2.1 The spent catalyst

Spent hydrocracking catalyst (Criterion HC-102 W/Ni/Al2O3/SiO2) was provided by National Iranian Oil Refining & Distribution Company (NIORDC). The spent catalyst was pre-treated by heating in a furnace at 600 $^{\circ}C$ for 4 hours. The decoked spent catalyst was gently dry ground and sieved. All spent catalysts used in this study were of particle size less than 150 μm.

2.2 Characterization of spent refinery hydroprocessing catalyst

Partial chemical composition was determined by a homemade method. 0.02 up to 0.05 *g* of sample was digested for 2 hours using 10 ml concentrated HNO_3 and10 ml concentrated HF then heated for about 2 hours up to 120 $^{\circ}C$. The sample was almost completely soluble. The digestate was cooled, filtered and made up to 100ml using deioniezed water and subjected to chemical analysis using an inductively-coupled plasma–optical emission spectrometer ICP-AES (Varian LIBERTY – RL).

2.3 Different methods of bioleaching

The acclimatized fungus from the final stage of adaptation with mixture of metal ions was cultured in PDA (potato dextrose agar (3.9 *%w/v*)) slant. In order to obtain sufficient numbers of spores, the culture was incubated at 30 $^{\circ}C$ for 5 days. The mature conidia were then washed off from the surface of the PDA medium using sterilized physiologic serum (9 g/L NaCl). The number of spores was counted using a Neubauer counting chamber and adjusted using sterilized physiologic serum to approximately 10^7 spores/ml. 2 mL of spore suspension was added to a 500 ml Erlenmeyer flasks containing 100 *mL* of sucrose medium with the composition: sucrose (100 g/L), $NaNO_3$ (1.5 g/L), KH_2PO_4 (0.5 g/L), $MgSO_4{\cdot}7H_2O$ (0.025 g/L), KCl (0.025 g/L) and yeast extract (1.6 g/L). The flasks were agitated in an incubator with orbital shaking at 120 rpm and at 30 $^{\circ}$C. Sterile experimental set-up was achieved by autoclaving at 121 $^{\circ}$C for 15 minutes prior to inoculation. Bioleaching was performed in 500 ml Erlenmeyer flasks with 100 ml of sucrose medium with the spent catalyst at various pulp densities (1, 2, 3, 4 and 5 %w/v). All experiments were carried out in an orbital shaking incubator at 30±1 $^{\circ}$C and 120 rpm. Three Different methods of bioleaching were carried out: (i) the fungus was incubated together with the medium and spent catalyst (one-step bioleaching), (ii) the fungus was first cultured in sucrose medium without spent catalyst for 4 days, after a sudden reduction in pH (beginning of organic acid production), sterilized catalyst was added (two-step bioleaching), and (iii) the fungus was first cultured in sucrose medium for 14 days. Then the suspensions were filtered through MN 640d and 0.2 μm (Millipore) filter paper, respectively, to obtain the cell-free spent

medium, and the filtrate that contained bio- produced metabolites was used for the leaching of spent sterilized catalyst added to the filtrate (spent medium leaching). Control experiments were conducted using fresh sucrose medium.

2.4 Analytical Methods

After the desired bioleaching time, the culture from each flask was filtered and the filtrate was analyzed for organic acids (i.e. citric, oxalic and gluconic acids) using high performance liquid chromatography (HPLC). Metal ions were analyzed using an ICP-AES (Varian LIBERTY – RL). Extracting and measuring of biomass-accumulated and associated metals, was performed as described by Santhiya and Ting (2006). The Scanning Electron Microscope was used to observe the morphology of the catalysts.

3. Results and discussion

3.1 Comparison of different methods of bioleaching

Prior to bioleaching experiments, pure cultures of adapted *Penecillum simplicissimum* were incubated under identical condition of bioleaching and investigated over 30 days in order to determine the optimum time for addition of catalyst in two-step bioleaching and filtration of the culture in the spent medium bioleaching. The increase in acid and biomass concentration, and the substantial hydrolysis of sucrose at the 4^{th} day, of incubation indicated that *Penecillum simplicissimum* was in the active growth phase. Thus, the spent catalyst was added to the culture for bioleaching after 4 days of incubation (under the two-step process). As 14 days of incubation marked the end of the active growth phase at which the gluconic acid concentration reached its maximum level and the spent medium was obtained by filtering the culture after this period.

Investigation of different methods in bioleaching of spent catalyst showed it is strongly influenced by the pulp density. The main agent in one-step and two-step and spent medium bioleaching was gluconic acid which was produced at pulp densities of more than 2 %w/v in one-step bioleaching and at pulp densities of more than 1 % w/v in two-step bioleaching (Table 1). The results of metal recovery showed that the optimum pulp density for spent catalyst bioleaching occurred at 1 % w/v in one-step (Figure 1), 3 % w/v in two-step (Figure 2) and 1% w/v in spent medium leaching (Figure 3). Metal leaching yield decreasing with increase in pulp density higher than optimum one in one-step and two-step method is due to the higher toxic metal concentration in spent medium as well as decrease in the initial pH of the spent catalyst suspensions. In the case of spent medium leaching, the decrease in leaching yield with increase in pulp density is likely to be due to the constant metabolite concentration in all pulp densities.

Two-step bioleaching has highest efficiencies for Fe and Ni at all pulp densities, with leaching efficiency at approximately 69.84-100 % Fe, and 50-70.2 % Ni.

The recovery yield in descending order for two-step and spent medium bioleaching are shown below, respectively, which are found to be slightly different.

$$Fe > Ni \approx W \approx Mo > Al \quad (1)$$

$$W \approx Fe \approx Mo > Ni > Al \quad (2)$$

Table 1: Organic acid concentration in different methods of bioleaching

organic acids mg/L	*One- Step* [(a)]					*Two- Step* [(a)]					*Spent Medium* [(b)]
	1%	*2%*	*3%*	*4%*	*5%*	*1%*	*2%*	*3%*	*4%*	*5%*	
Oxalic acid	<1	32	4	54	36	<1	<1	<1	18	10	<1
Citric acid	791	197	<1	<1	<1	498	<1	<1	32	<1	<1
Gluconic acid	<1	<1	235	660	1192	<1	234	1381	885	116	1350

[(a)] *After 30 days of incubation in the presence of spent catalyst*
[(b)] *After 14 days of incubation in the absence of spent catalyst*

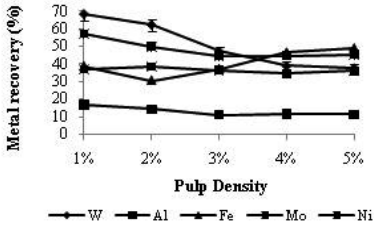

Figure 1: Metal recovery at different pulp densities in one-step method

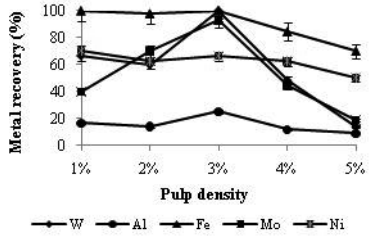

Figure 2: Metal recovery at different pulp densities in two-step method

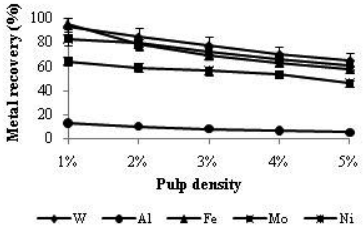

Figure 3: Metal recovery at different pulp densities in spent medium method

Spent medium leaching consistently resulted in the higher metal leaching efficiency than that of one-step bioleaching for all metals except for Al (Figure 4). This is possibly due to the higher red pigment concentration in one-step bioleaching compare to spent medium leaching. This compound has a hemiquinonoid structure and resembles aluminum complexants (Rezza et al., 2001), therefore, this compound could possibly act as a leaching agent. Figure 4, shows that two- step bioleaching at optimum pulp density

gave maximum extraction yields which the amounts of leached metals were 100 % of W, 100 % of Fe, 92.7 % of Mo, 66.43 % of Ni, and 25 % of Al.
In control experiments (using fresh medium), the recovery yield of Al, and Ni is found to be negligible under all pulp densities. While, depending on the pulp density, the fresh medium effected an extraction of 8-13.4 % W, 6.5-11.9 % Mo, and 14.5-19.5 % Fe. The behaviour of Fe leaching was different from that of W and Mo; by increasing the pulp density and consequently decreasing in pH (from 4.82 to 4.2) extraction yield of Fe decreased in good agreement with Wu and Ting (2006), while W and Mo extraction increased.

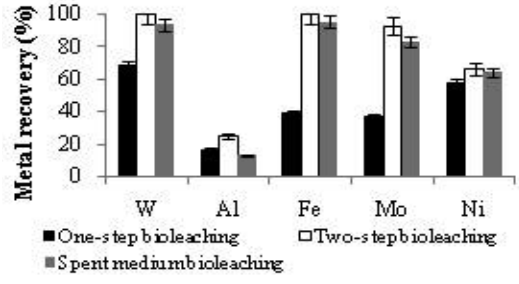

Figure 4: Metal recovery at optimum pulp density in different bioleaching methods

Figure 5, shows the SEM photomicrograph of the spent and bioleached catalyst. The absence of the fine particles in the bioleached catalyst is possibly due to dilution under the effect of bioleaching. Surface morphology of spent and bioleached catalyst is evident in (Figure 5a, b). The attached fine particles and deposits on spent catalyst surface (Figure 5a) are gone due to the effect of bioleaching (Figure 5b).

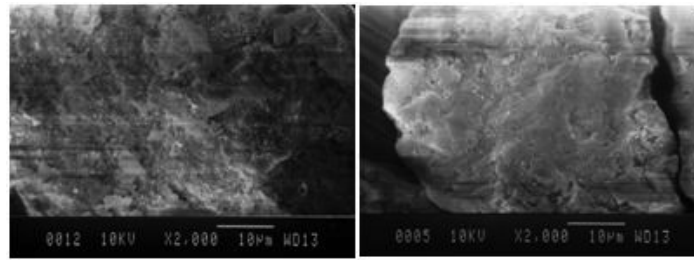

Figure 5: SEM photomicrograph of spent and bioleached catalysts: (a) spent catalyst (2000× magnification), (b) bioleached catalyst (2000× magnification)

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