

Biotechnologies for the Valorisation of Spent Refinery Catalysts and Recovery of Ni, V and Mo

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This paper deals with bioleaching of metals from hazardous spent hydro-processing catalyst by means of iron/sulphur oxidizing bacteria. The exhaust catalyst was rich in nickel (45 mg/g), vanadium (44 mg/g) and molybdenum (94 mg/g). Before bioleaching, the solid was washed by means of a mixture of Tween 80 and ethyl alcohol, for hydrocarbons removal. The effects of elemental sulphur, ferrous iron and actions contrasting a possible metal toxicity (either the presence of powdered activated charcoal or the simulation of a cross current process by means of filtration stages in series) was investigated. Ferrous iron resulted to be essential for metals extraction and for bacteria adaptation. Nickel and vanadium were successfully bioleached in the presence of iron, reaching extraction yields of 83% and 90%, respectively; on the other hand extractions around 50% for nickel and vanadium were observed both in biological systems in the absence of iron and in the chemical controls with iron. As concerns molybdenum, the highest extraction yields experimentally observed for molybdenum was about 50%, after 21 days bioleaching in the presence of iron, while a maximum extraction of 25 % was observed in the other treatments. In conclusion, a bio-oxidative attack with iron could successfully extract nickel, vanadium and partially molybdenum. Further actions aimed at contrasting a possible metal toxicity resulted not to be effective and partially inhibited the metal extraction processes.

1. Introduction

Spent catalysts represent a large amount of refinery solid waste. In particular, hydro-processing catalysts contain base valuable metals, such as nickel, vanadium and molybdenum and for their toxic component, these wastes have been classified as hazardous by the Environmental Protection Agency in the USA (Furimsky, 1996). Since their base valuable metal content, replace in discharge this kind of waste represents not only an environmental threat but an important economical loss, too. To avoid pollution in land disposal as well as minimise landfill space, the spent catalysts are subjected to metal extraction by various solubilization process and reused in a variety of

applications. Worldwide, several companies are involved in metal reclamation from spent hydroprocessing catalysts; their technologies are based on two principal approaches: either hydrometallurgy or pyrometallurgy. With the hydrometallurgical approach metals are leached by means of catalysis with acids or bases, while pyrometallurgy uses a heat treatment, such as roasting and smelting (Marafi and Stanislaus, 2003). In comparison with this kind of technologies, biotechnological leaching processes offer attractive features: processes are more cost efficient, simpler and more environmentally friendly than their chemical counterparts (Aung and Ting, 2005; Santhiya and Ting, 2005). The development of an innovative eco-sustainable process for the valorisation of such wastes would undoubtedly give significant advantages to environment and to primary resources preservation.

In this paper, a biotechnological environmentally friendly strategy, involving bioleaching abilities of Fe/S oxidizing bacteria has been applied on spent hydro-processing catalyst, wastes produced by Italian refineries. A full factorial experiment was implemented the three main experimental factors were: the presence of elemental sulphur, the presence of ferrous iron and the application of strategies hampering an eventual toxic effect of the high concentration of metals.

2. Materials and Methods

2.1 The exhaust catalyst

The Lc Finer catalyst is a waste coming from an Italian refinery. Valuable metals content was estimated at 4,5%, 4,4% e 9,4% (w/w) for Ni, Mo and V, respectively. X-ray diffraction analysis (Siemens D-500 diffractometer) revealed the presence of Ni_3S_4 (polydymite), NiV_2S_4 (nickel vanadium sulphide), Mo_4O_{11} (molybdenum oxide). The organic content was about 15% (w/w).

2.2 Microorganisms

A mixed culture of three strains of Fe/S oxidizing bacteria (*Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans* and *Leptospirillum ferrooxidans*) isolated from an environmental sample was kindly provided by Prof. Groudev (Department of Engineering and Geoecology, University of Mining and Geology "Saint Ivan Rilski", Sofia, Bulgaria). This culture was cultivated under acidic condition (pH 2), in the ideal liquid growth medium 9K (Silverman and Lundgren, 1959).

2.3 Catalyst pre-treatment

The exhaust catalyst was washed by an aqueous solution of ethyl alcohol 1% (v/v) and Tween 80 (sorbitan mono-oleate ethoxylated with 20 moles of ethylene oxide) 0,1% (v/v). The solid (5% w/v) was suspended in 1 L solution under magnetic agitation, under room temperature for 24 h. A rough estimate of organic carbon dissolution by COD determination (dichromate/ H_2SO_4 ; Photometer PC MULTI Direct) revealed that an hydrocarbons extraction yield of about 30% was achieved. Washing with only deionised water under the same operating conditions did not dissolve significant hydrocarbons. At the end of washing, catalysts were filtered, dried and stored at room temperature for next bioleaching tests.

Table 1. Factors and levels investigated for exhaust catalysts bioleaching

Factors	Levels		
Elemental sulphur (0,1%)	no		yes
Ferrous ion (160 mM)	no		yes
Hampering toxicity action	no	activated carbon	seq. filtration

2.4 Bioleaching experiments

Experiments were carried out in autoclaved 250 mL Pyrex flasks filled to a volume of 100 mL, in order to assure oxygen transfer. Incubation was carried out in an orbital thermostated incubator (S150, Stuart), at 30°C and 175 rpm shaking. Catalyst concentration was 10g/L and the medium composition was as a 9K modified according to experimental conditions. Periodically pH was monitored and aliquot amounts (1.5 mL) were sampled for metals determination in solution after centrifugation at 8000 g x 5 min. Table 1 shows factors and levels investigated, while Table 2 shows all treatments in details, according to a full factorial experiment. For each bioleaching treatment in Table 2, a chemical control test was also performed with no bacteria inoculum. Where specified, powdered activated carbon (PAC; Powdered Activated Charcoal Norit, 05100, Fluka) was added in a mass ratio 1:10 carbon:catalyst. Filtration was performed as a possible hampering toxicity action by filtering (0,22 µm; Millipore membranes) every 7 days the suspension and re-suspending the cake (bearing both catalysts and bacteria) in fresh medium.

2.5 Analytical determinations

pH was determined by Inolab Multi 720 (WTW). Soluble iron (II) and total soluble iron were determined spectrophotometrically (PPST method, with a additional reducing phase for determination of total soluble iron, Photometer PC MULTI Direct). Ferric iron was determined by difference. Molybdenum, nickel, vanadium and aluminium were determined by atomic absorption spectrometry (Varian Spectra AA 200).

Table 2. Full factorial plan (factors and levels in Table 1)

Treatments	Elemental sulphur	Ferrous ion	Hampering toxicity action
1	no	no	no
2	yes	no	no
3	no	yes	no
4	yes	yes	no
5	no	no	activated carbon
6	yes	no	activated carbon
7	no	yes	activated carbon
8	yes	yes	activated carbon
9	no	no	seq. filtration
10	yes	no	seq. filtration
11	no	yes	seq. filtration
12	yes	yes	seq. filtration

3. Results and Discussion

The main factors considered during the experimental investigation for the recovery of metals from spent refinery catalysts were (Table 1) elemental sulphur, ferrous iron and the application of strategies hampering an eventual toxic effect of highly concentrated metals. These strategies were applied either adding activated carbon or simulating a cross current system by a periodic filtration of the liquor leach and were experimented since metal concentrations in the spent catalyst were supposed to be too high even for highly resistant bacteria as *Thiobacilli* spp. (Tuovinen et al., 1971).

Figure 1 shows the metals extraction yields experimentally determined both in inoculated experiments and in their respective controls (see Table 2). It is evident that a biological effect on metals solubilisation is significant only in the presence of ferrous iron: in fact in all tests with ferrous iron the biological treatments showed extraction yields much higher than the respective controls. In particular, nickel and vanadium were successfully bioleached in the presence of iron, reaching extraction yields of 83% and 90%, respectively; on the other hand extractions around 50% for nickel and vanadium were observed both in biological systems in the absence of iron and in the chemical controls with iron. As concerns molybdenum, the highest extraction yields experimentally observed for molybdenum was about 50%, after 21 days bioleaching in the presence of iron, while a maximum extraction of 25 % was observed in the other treatments.

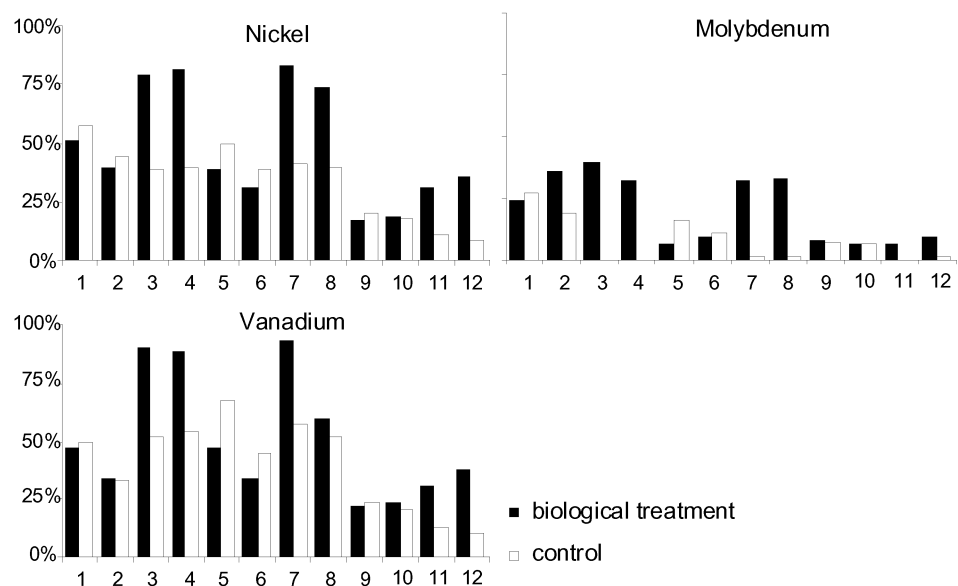


Figure 1. Metal extraction yields at the end (21 d) of the biological treatments and their respective controls (see Table 2 for treatments operating conditions).

Figure 2 shows metal extraction yields vs. time profiles in all treatments in the presence of iron. It can be observed that nickel and vanadium dissolution kinetics in the presence of iron are significantly higher than molybdenum kinetics. Appreciable extraction yields have been achieved just after 7 days of treatment for both Ni and V, while Mo dissolution seems to be slower. This is probably due to different speciation of the three metals inside the solid matrix. Experimental data in Figures 1 and 2 also suggest that there is not a significant effect of the presence of activated carbons, while the periodic filtration of the liquor leach (treatments 11 and 12) seems even to inhibit the metals dissolution. These results have also been confirmed by an analysis of the variance (Montgomery, 1991), as reported in Figure 3 for nickel and molybdenum extraction yields as responses. All the achieved results suggested that the indirect mechanism seems to be the main responsible for metals leaching (Vegliò et al., 1999): Ni and V dissolution, that is due to sulphides oxidation, is probably not carried out directly by bacteria adsorbed onto the solid surface but mainly by the ferric iron produced in the aqueous phase by the biological oxidation of the ferrous iron. Molybdenum dissolution might follow a different mechanism due to its different speciation and to a reduction necessary for its dissolution. Further work is in progress to confirm these hypotheses.

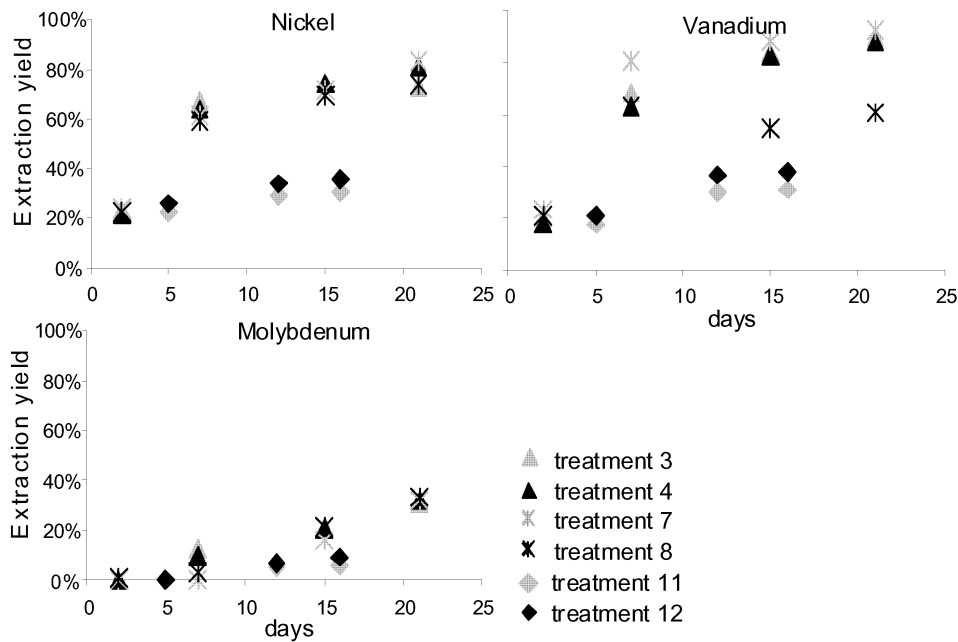


Figure 2. Metal extraction yields vs. time profiles in the presence of Fe^{2+} (see Table 2 for treatments operating conditions).

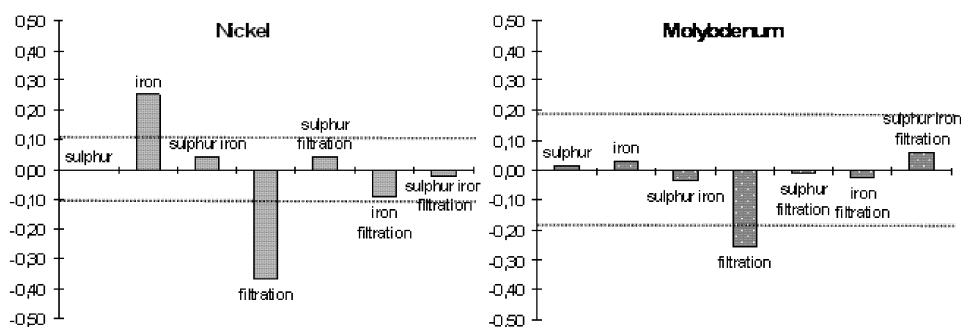


Figure 3. Main effect and interactions on nickel and vanadium extraction yields (experimental data in Figure 1). Dotted lines represent the 95% significant effects.

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