

Bioleaching of nickel, vanadium and molybdenum from spent refinery catalysts

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Abstract. 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. The development of an innovative eco-sustainable process for the valorisation of such wastes would undoubtedly give significant advantages also taking into account primary resources preservation. 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 hydrocarbon 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 metal 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 was about 50%, after 26 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.

Introduction

Spent catalysts represent a large amount of refinery solid waste. In particular, hydro-processing catalysts usually consist of molybdenum (Mo) supported on an alumina carrier with promoters such as cobalt (Co) or nickel (Ni). Catalysts deactivate with time and need a regeneration process; after a few cycles of regeneration and reuse, their activity may decrease and further regeneration may not be economically feasible [1,2], so they are discharged as solid waste. For their toxic component, these waste have been classified as hazardous by Environmental Protection Agency in the USA [3]. The spent catalysts discarded from the hydro-processing units usually contain 7-20 % V+Ni, 15-25 % coke, 7-15 % sulphur , 5-10 % residual oil together with active metals (Mo and Co or Ni) and Al₂O₃ originally present in the catalyst [4]. These metals are highly valuable for their extensive use in the steel industry and in the manufacture of special alloys, so replace in discharge this kind of waste represents not only an environmental threat but an important economical loss, too. Spent hydroprocessing catalysts could be used as a cheap source for these valuable metals. To avoid pollution in land disposal as well as minimise landfill space, 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 this kind of waste; their technologies are based on the hydrometallurgical approach, metals are leached with acids or bases, or on the pyrometallurgy one, that uses a heat treatment [5]. 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 [6,7].

In this paper, a biotechnological environmentally friendly strategy, involving bioleaching abilities of Fe/S oxidizing bacteria has been applied on spent hydro-processing catalyst from 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.

Materials and Methods

The exhaust catalyst. The Lc Finer catalyst used in the present work came from an Italian refinery. Ni, Mo and V content was estimated at 4.5%, 4.4% e 9.4% (w/w), respectively. X-ray diffraction analysis (Siemens D-500 diffractometer) revealed the presence of Ni₃S₄ (polydymite), NiV₂S₄ (nickel vanadium sulphide), Mo₄O₁₁ (molybdenum oxide). The organic content was about 15%.

Microorganisms. A mixed culture of three strains of Fe/S oxidizing bacteria (*Acidithiobacillus ferrooxidans*, *A. thiooxidans* and *Leptospirillum ferrooxidans*) isolated from an environmental sample was kindly provided by Prof. Groudev (Department of Engineering and Geocology, 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 [8].

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 under magnetic agitation, at room temperature for 24 h. A rough estimate of organic carbon dissolution by COD determination (dichromate/H₂SO₄; Photometer PC MULTI Direct) revealed a hydrocarbons extraction yield of about 30%. At the end of washing, catalysts were filtered, dried and stored at room temperature for further bioleaching tests.

Bioleaching experiments. Experiments were carried out in autoclaved 250 mL Pyrex flasks, with a volume of 100 mL, 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 (Inolab Multi 720 WTW) and aliquot amounts (1.5 mL) were sampled for metals determination in solution after centrifugation at 8000 g x 5 min. Factors and levels investigated are shown in Table 1. For each bioleaching treatment (Tab. 2), a chemical control test was also performed with no bacteria; all microcosms were replicated twice. Where specified, powdered activated carbon (PAC; Powdered Activated Charcoal Norit, 05100, Fluka) was added in a mass ratio 1:10 carbon:catalyst, or a 7 days periodic filtration (0,22 µm; Millipore membranes) was operated and the cake re-suspended in fresh medium.

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

Table 1. Factors and levels investigated for exhaust catalysts bioleaching.

Mo, Ni and V were determined by atomic absorption spectrometry (Varian Spectra AA 200), while soluble iron and total soluble iron were determined by PPST method, with a reducing phase for the total soluble iron (Photometer PC MULTI Direct); ferric iron was determined by difference.

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	PAC
6	Yes	no	PAC
7	No	yes	PAC
8	Yes	yes	PAC
9	No	no	seq. filtration
10	Yes	no	seq. filtration
11	No	yes	seq. filtration
12	Yes	yes	seq. filtration

Table 2. Factorial plan (factors and levels in Table 1).

Results and Discussion

The main factors considered during the catalysts bioleaching experiments were: elemental sulphur, ferrous iron and the application of strategies hampering an eventual toxic effect of highly concentrated metals (either adding activated carbon or simulating a cross current system by a periodic filtration of the liquor leach). These operations were supposed to be effective because the metal concentrations in the spent catalyst were probably too high even for highly resistant bacteria as *Thiobacilli* spp. [9].

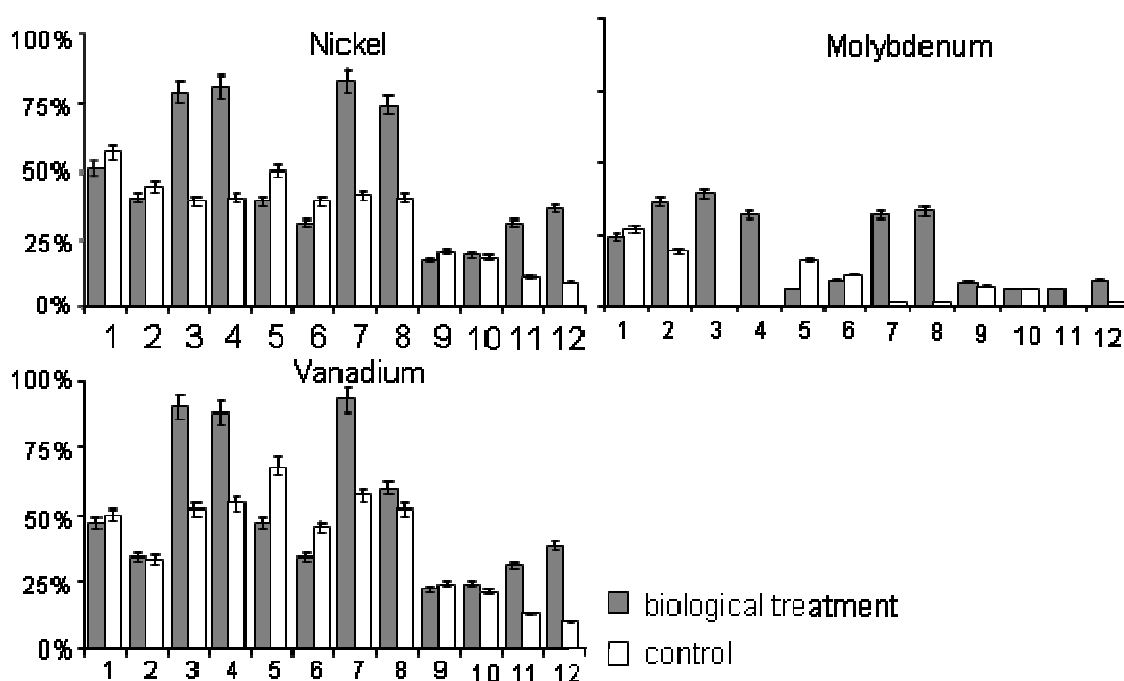


Figure 1. Metal extraction yields at the end (21 d) of the biological treatments and their respective controls (see Table 2 for treatments operating conditions).

The metal extraction yields in the planned experiments and their controls are shown in Figure 1. It was evident that a biological effect on metal solubilization is significant only in the presence of ferrous iron: in all tests with ferrous iron the biological treatments had extraction yields higher than in their controls: Ni and V were successfully bioleached in the presence of iron, reaching extraction yields of 83% and 90%, respectively; on the other hand, extractions around 50% for Ni and V were

observed both in biological systems in the absence of iron and in the chemical controls with iron. As concerns Mo, the highest extraction yields experimentally observed about 50%, after 21 days bioleaching with iron, while a maximum extraction of 25 % was observed in the other treatments. It could be observed that Ni and V dissolution kinetics in the presence of iron are significantly higher than Mo kinetics. For Ni and V appreciable extraction yields have been achieved just after 7 days of treatment, while Mo dissolution seemed to be slower (data not shown). This was probably due to different speciation of the three metals inside the spent catalyst. Experiments also showed that there was 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 (Fig. 1). This may suggest that bacteria were not inhibited by the presence of dissolved metals and consequently it was not useful to apply any strategy aimed at hampering metal toxicity. Furthermore, the negative effect of the periodic filtration can suggest that soluble metabolites are also involved in metal leaching. An analysis of the variance [10] confirmed these results (data not shown). Results illustrated above suggest that the indirect mechanism could be the main responsible for metals leaching [11]: Ni and V were, in fact, present as sulphides, whose oxidation is probably not carried out directly by bacteria but mainly by the ferric iron produced in the aqueous phase by the biological oxidation of the ferrous iron. Because of its speciation, Mo dissolution might follow a different mechanism: not an oxidation but a reduction is necessary for its dissolution. In conclusion, this paper showed that a bio-oxidative attack in the presence of iron could successfully extract nickel, vanadium and partially molybdenum. The observed results suggested that the indirect mechanism seems to be the main responsible for metals leaching: metals might be dissolved by a chemical attack of the bio-oxidated ferric iron rather than by a direct biological attack.

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