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Fungal Leaching of Hazardous Heavy Metals from a Spent Hydrotreating Catalyst

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***Abstract*—**In this study, the ability of *Aspergillus niger* and *Penicillium simplicissimum* to extract heavy metals from a spent refinery catalyst was investigated. For the first step, a spent processing catalyst from one of the oil refineries in Iran was physically and chemically characterized. *Aspergillus niger* and *Penicillium simplicissimum* were used to mobilize Al/Co/Mo/Ni from hazardous spent catalysts. The fungi were adapted to the mixture of metals at 100-800 mg L^{-1} with increments in concentration of 100 mg L^{-1}. Bioleaching experiments were carried out in batch cultures. To investigate the production of organic acids in sucrose medium, analyses of the culture medium by HPLC were performed at specific time intervals after inoculation. The results obtained from Inductive coupled plasma-optical emission spectrometry (ICP-OES) showed that after the one-step bioleaching process using *Aspergillus niger*, maximum removal efficiencies of 27%, 66%, 62% and 38% were achieved for Al, Co, Mo and Ni, respectively. However, the highest removal efficiencies using *Penicillium simplicissimum* were of 32%, 67%, 65% and 38% for Al, Co, Mo and Ni, respectively

***Keywords*—**Aspergillus niger, Bioleaching, Heavy metals, Penicillium simplicissimum, Spent catalyst

I. Introduction

EXTENSIVELY used in the petroleum industry, refinery solid catalysts [12] contain metals such as Al, V, Mo, Fe, Sn, Co and Ni, which facilitate different hydrocarbon transformations[15]. Spent catalysts contribute significantly to the amounts of solid wastes generated in the petrochemical industry. Hydroprocessing, reforming, and desulfurization all produce spent catalysts as major industrial waste. The principal metal contaminants in these various types of catalysts are Ni, Co, and Mo [22].The catalysts have a definite shelf life and deactivate with time; in fact, they often require replacement after two to three years of operation [7]. The storage of spent petroleum catalysts has never been a suitable option. The only alternative is to establish suitable, economical, eco-friendly metal recovery processes for the spent petroleum catalyst [13].Bioleaching processes are based on the ability of microorganisms (bacteria or fungi) to transform solid compounds; the transformation occurs via the production of organic or inorganic acids, which results in soluble and extractable elements that can be recovered. Bioleaching can be considered an example of "clean technology" given its associated lower cost and energy requirements when compared with non-biological processes [10].

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Bioleaching also offers good prospects for recovering valuable metals while generating considerably less environmental pollution.The most common microorganisms capable of metal solubilization include bacteria such as *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans,* as well as fungi of the *Aspergillus* and *Penicillium* genera [1]. The mechanisms potentially involved in bioleaching include (i) acidolysis; (ii) complexolysis; (iii) redoxolysis; and (iv) bioaccumulation [20]. Compared to bacterial leaching, fungal leaching has the following advantages: (i) The ability to grow under higher pH, favoring the bioleaching of alkaline solid wastes; (ii) a generally faster leaching process with a shorter lag phase; and (iii) the ability of excreted metabolites (e.g., organic acids) to form complexes with metal ions, thus reducing the toxicity of the metabolites to the biomass [5]. The use of *Aspergillus niger* for the bioleaching of the spent fluid catalytic cracking (FCC) and spent refinery processing catalysts has also been reported [1]. However, the operating costs are relatively higher for fungal leaching (by hetrotrophs) compared to bacterial leaching (by autotrophs) given the requirement of an organic carbon source for their growth and organic acid excretion. Acidolysis is the principal mechanism in the bioleaching process using *Aspergillus niger*; the fungus has been reported to produce organic acids, including citric, oxalic and gluconic acids, during bioleaching [5].Low pH favors acidolysis and is followed by the release and enhanced mobility of free metal cations by protonation [17].

Repeated subcultivations of microorganisms to increase the concentrations of heavy metals may allow the isolation of heavy metal-tolerant mutants [21]. The adaptation of acclimatized microorganisms to relatively high heavy metal concentrations has often been attributed to the activation of alternative biochemical cellular growth-promoting pathways [14]. In this work, the fungi *A. niger* and *P. simplicissimum* were adapted to a mixture of Al, Co, Mo and Ni (at 100-800 mg L^{-1} with increments of 100 mg L^{-1}). Although the process of metal leaching using *A. niger* looks promising, however there is a lack of studies about leaching heavy metals from spent refinery catalysts by using *A. niger* and *P. simplicissimum* under five optimized variables.

Bioleaching of the spent catalyst was conducted using the various adapted strains. The growth of the adapted fungi was monitored, along with the extracted metals from the spent catalyst and the organic acids excreted by the various strains. Extraction efficiencies of the metals using the fungi under optimum values were also compared with each other.

II. Materials and Methods

A. Spent refinery Processing Catalyst

The spent refinery processing catalyst (UOP: S-12 $Co/Mo/Al_2O_3$) was provided by one of the oil refineries in Iran (Naphtha Treater unit). The catalyst was extrudate in shape and approximately 1.2 mm in diameter; its surface area and pore volume were 210 m^2/g and 0.5 cm^3/g, respectively. The spent catalyst was gently dry-ground using a porcelain mortar and pestle and analyzed by dry screening through a British Standard Specifications (BSS) sieve.

B. Fungal Strains and Growth Conditions

The fungi were obtained from Institute of Chemical and Biomolecular Engineering, National University of Singapore. They were cultivated on 3.9% (w/v) potato dextrose agar (Becton Dickinson, USA) plates and were kept in an incubator for 7 days at 30°C. Seven-day old conidia were harvested from the surface of potato dextrose agar using sterile deionized water. The number of spores was counted under an optical microscope (Olympus BH-2) at 400× magnification using a hemacytometer. The spore suspension was diluted with deionized water to the desired spore suspension concentration of 10^7 spores mL^{-1}. The pH of the solution was measured using a pH meter (pH lab, model 827) at regular time intervals.The bioleaching experiments were carried out by adding 1 mL of spore suspension (1×10^7 spores mL^{-1}) into 500 mL Erlenmeyer flasks containing 100 mL of sucrose medium (Merck) with the following composition: sucrose (100 g L^{-1}), $NaNO_3$ (1.5 g L^{-1}), KH_2PO_4 (0.5 g L^{-1}), $MgSO_4.7H_2O$ (0.025 g L^{-1}), KCl (0.025 g L^{-1}) and yeast extract (1.6 g L^{-1}). Leaching was carried out for a period of 30 days and under optimized values of pH, temperature, pulp density, percent of inoculation and rotation speed. At regular time intervals, the growth characteristics of the fungi and the concentration of metal values in the filtrate were determined in the bioleaching process. Control experiments were also conducted using deionised water and sucrose medium in the presence of the catalyst.

C. Analytical methods

HPLC Analysis: Generally speaking, bioleaching using organic acids produced by *A. niger* and *P. simplicissimum* would be more effective than chemical leaching using organic acid agents because of the higher removal efficiencies and lower cost of the leaching agents [16]. The organic acids produced were analyzed by HPLC (HP 1100 series) with UV (210 nm) and RI detectors, and were conducted by the Iran Mineral Processing Research Center (IMPRC).

Analysis of Metal Composition: ICP-OES with standard procedures was used to analyze the metals in the bioleaching process after acid digestion of the samples. For partial chemical composition, 1 g of the spent catalyst was digested for 2 h using concentrated hydrochloric acid and nitric acid in a ratio of 3:1. The digestate was cooled, filtered through Whatman 42 filter paper, made up to 100 mL using 50% HCl and subjected to metal analysis [18]; this procedure was conducted by the IMPRC.

Statistical Analysis: All experiments were conducted in duplicate. Data points in figures represent means with error bars shown (± S.D.). A three level CCD was performed using the statistical software (Design-Expert 7.1.4 Stat-Ease Inc., Minneapolis, MN) to analyze the significance of experimental results (with 95% level of confidence, $\alpha = 0.05$) [11].

III. Results and Discussion

Characterization of the Spent Refinery Processing Catalyst: Chemical analysis of the spent refinery processing catalyst revealed the presence of 39.4 % of Al, 8% of Mo, 2.4% of Co and 0.06% of Ni in the catalyst, all of which were in the oxide form of the metal. The metal concentrations in these samples were extremely high, posing a significant hazard for human health and the environment. The elements present in the spent catalyst were analyzed by ICP-OES, as summarized in Table 1.

Determination of the Catalyst Surface Morphology by SEM : The SEM photomicrograph (XL30, Philips) of the spent refinery catalyst (Fig. 1a) using the Particle Size Analyzer revealed the extrudal shape of the catalyst with considerable variation in particle size. The bioleached spent catalyst using *A. niger* (Fig. 1b) showed small broken particles, possibly due to the effect of bioleaching.

Bioleaching Studies; Removal of heavy metals in the one-step Process using A. Niger and P. Simplicissimum: One-step process experiments were performed by growing *A. niger* in the presence of the spent catalyst at a pulp density of 2 g L^{-1}, using a 12 percent inoculum (w/v), a speed of 115 rpm, pH of 5.00 and temperature of 31°C, i.e., at the optimized values which were obtained by response surface methodology [11]. In another experiment parallel to the research on *A. niger*, *P. simplicissimum* was grown in the presence of the spent catalyst at a pulp density of 2 g L^{-1}, using a 9 percent inoculum (w/v), rotation speed of 122, pH of 5.50 and temperature of 32°C [11]. The pH and concentrations of Al, Co, Mo and Ni were determined at regular time intervals to obtain the extraction efficiency of the metals. Figure 2a depicts the pH profiles of the medium in the presence and absence of *A. niger* in the presence of the spent refinery catalyst samples under optimized conditions. Similar trends were also observed for *P. simplicissimum* (Fig. 2b). In the control experiments (only culture medium without fungi), the pH decreased steadily from the initial value of 5.00 to 4.80 and then increased to 5.58 for *A. niger*. For *P. simplicissimum* pH decreased from 5.50 to 5.20 and then increased to 5.45 at the end of the 30-day incubation. From Figs. 2a and b, it is clear that the pH decreased from an initial value of 5.00 to 3.96 in the case of *A. niger* and from 5.50 to 5.20 and then increases to 5.5 at the end of the 30-day incubation in the case of *P. simplicissimum*; this demonstrated that the addition of the contaminated spent catalyst resulted in some toxicity to fungal growth. The decrease in pH of the medium was mainly caused by the excreted metabolites produced by the fungi; the metabolites included H^+ and organic acids (citric, gluconic,

oxalic) [5]. Increase of the pH after 12-days of the addition of catalyst in the bioleaching process by P. *simplicissimum* could be due to the slightly alkaline nature of the catalyst added or this was due to the reason that after complete utilization of glucose, the fungi started to use its own metabolites. The HPLC results demonstrated that the amount of gluconic acid produced by *A. niger* was higher than in *P. simplicissimum*, in which the amount of citric acid was higher. The pH increase after 12 days of the addition of the catalyst in the bioleaching process by *A. niger* could be due to the slightly alkaline nature of the catalyst added. Compared to the control experiments, the reduction of pH in bioleaching processes was greater.

Production of Organic Acids: The leaching process using fungal microorganisms is based on the complexation of metals by the excreted organic acids and on the bioaccumulation of metals by the organism's mycelia. To confirm that *A. niger* and *P. simplicissimum* were indeed producing organic acids in the sucrose medium, HPLC analyses of the culture medium were performed at specific time intervals after the inoculation. In the case of *A. niger,* gluconic acid was produced at the highest concentration (2676.4 mg L^{-1}) after 30 days of inoculation (1392.4 mg L^{-1} were produced after 20 days of inoculation), followed by citric acid (922.5 mg L^{-1}) and oxalic acid (474.9 mg L^{-1}), which were produced under similar optimal conditions as the optimized values of the leached metals. The optimal time for the addition of spent catalyst for gluconic acid production is 0 days. This is consistent with the fact gluconic production is optimal at a high pH. In the latter 5 days of the bioleaching process, the liberation of metal oxides from the alumina matrix increased. Hence, the exposure of the fungus to theses toxic metals (Al, Co, Mo and Ni) also increased. In order to reduce the toxicity of these metal ions, excretion of gluconic acid increased whereas citric acid and oxalic acid concentration decreased. In the case of *P. simplicissimum*, the concentration of citric acid secretion was very much higher (4282.6 mg L^{-1}) in the presence of the spent catalyst followed by oxalic acid (108.4 mg L^{-1}); a negligible amount of gluconic acid was produced after 30 days of inoculation. The fungi transform insoluble metal compounds into insoluble metal oxalates via an intermediate solubilization process. The concentrations of organic acids excreted by the fungi during the one-step process are shown in Fig. 3 (a-b). It is well known that in the presence of toxic metals, the fungus ameliorates the toxic effects of metals through complexation or precipitation by excreted metabolites [8]. The higher accumulation of oxalic acid by *A. niger* respect to *P. simplicissimum* in the presence of spent catalyst is mainly due to the induction of the enzyme oxaloacetate hydrolase and the presence of heavy metals, such as Co, Mo and Ni. Bioleaching using both fungi is mainly based on the acidolysis mechanism, i.e., the solubilization of the material on account of the acidification [9]. Using *A. niger* in the one-step bioleaching process resulted in the concentration of oxalic and citric acids remaining low, but not that of gluconic acid; in the case of *P. simplicissimum*, the concentration of citric acid was the highest compared to other two organic acids produced. It has been reported that the type and concentration of organic acids excreted by fungi depends on various factors including the buffering capacity, pH, carbon source and the presence of certain heavy metals and trace elements in the growth medium [3]. Although the mentioned acids are important leaching agents in the extraction of metals from equilibrium catalyst particles, their biosorption by fungal mycelium should not be underestimated [2].

Metal leaching Efficiency in one-step Bioleaching by A. niger and P. Simplicissimum: Some researchers reported that the increase in the leaching of heavy metals paralleled the increase in the concentration of organic acids (mainly citric acid). This phenomenon indicated that the biogenically produced organic acids played a direct and important role in the bioleaching process [1]. After 30 days under optimal conditions, a parallel increase in the concentration of acids and metals leached was observed and the concentration of metals extracted from the spent catalyst gradually increased with time. Therefore, the metal extraction efficiency of cobalt was the highest at 66% and 65% using *A. niger* and *P. simplicissimum*, respectively. It is apparent that dissolution of metals appears to be sluggish at the beginning of the leaching process and does not proceed significantly until after 12 days of leaching in which the highest metal leaching efficiencies were reached for all metals (Al, Co, Mo and Ni). The decrease in leaching efficiency beyond the maximum is probably due to the precipitation of unknown insoluble products (such as metal oxalate). The metal leaching efficiencies of the one-step process under optimal conditions during 30 days are shown in Fig. 4a and b for *A. niger* and *P. simplicissimum*, respectively. Figure 5 also shows the bioleaching yield of various metals in the spent catalyst retained by the fungi under optimum conditions. In both one-step bioleaching processes with *A. niger* and *P. simplicissimum*, the extraction yields of Al, Co, Mo and Ni were more or less similar (in the range of 27-32%, 65-67%, 62-63% and 38%, respectively). It was clear that the bioleaching recovery in the presence of the both microorganisms was approximately 20-30% higher than leaching without using the fungi, especially in the case of cobalt, in which the extraction yield was 70% more than that of the control experiment. The simultaneous increase in the concentration of gluconic acid and the metals (in the case of *A. niger*) and citric acid and metals (in the case of *P. simplicissimum*) indicated the acids produced by the fungus played a direct and important role in the bioleaching process. In fact, in our study, pH was taken as an indication of growth.

IV. Conclusions

The deposition of metal contaminants (e.g., Al, Co, Mo and Ni) on the catalyst causes a decrease in catalyst activity. Our findings indicate that the one-step bioleaching processes using either *A. niger* or *P. simplicissimum* could be effective for the bioleaching of heavy metals from spent refinery catalysts (Co-Mo type). In addition, the latter processes are examples of promising technology for the biological detoxification of spent catalysts. For *A. niger* an increase in the concentration of gluconate increased the bioleaching of metals from the spent catalyst, hence it was the gluconic acid which played a major

role in the bioleaching of metals. In contrast, citrate was predominant in bioleaching of metals by *P. simplicissimum*. The present investigation has shown that the highest extraction of metal values from the spent refinery catalyst (27% Al, 66% Co, 62% Mo and 38% Ni) were obtained in bioleaching by *A. niger* and (32% Al, 67% Co, 65% Mo and 38% Ni) in bioleaching by *P. simplicissimum* under optimal conditions in 30 days. We speculate that the attachment of fungi to the surface of the catalyst particles probably caused the increase in the local acid concentration on the catalyst surface. The higher local acid concentration may enhance the solubilization of the metals deposited on the surface of the catalysts. Some of the solubilized metals can be biosorbed by the fungi, when they are in close contact with the catalyst particles. Performing repetitions of the bioleaching process would increase the metal recovery from the spent catalysts, but this would make the process even slower and more expensive compared to a single-step bioleaching process.

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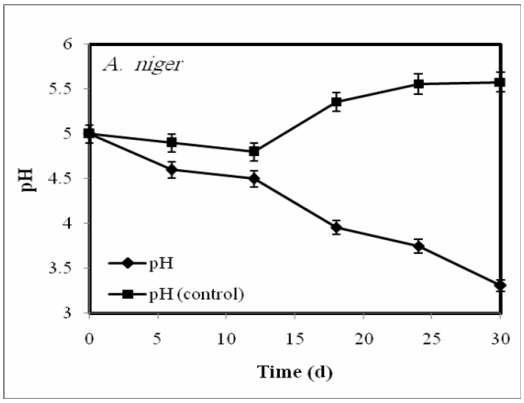
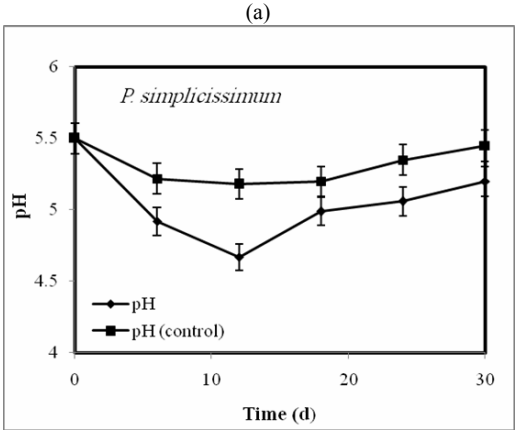
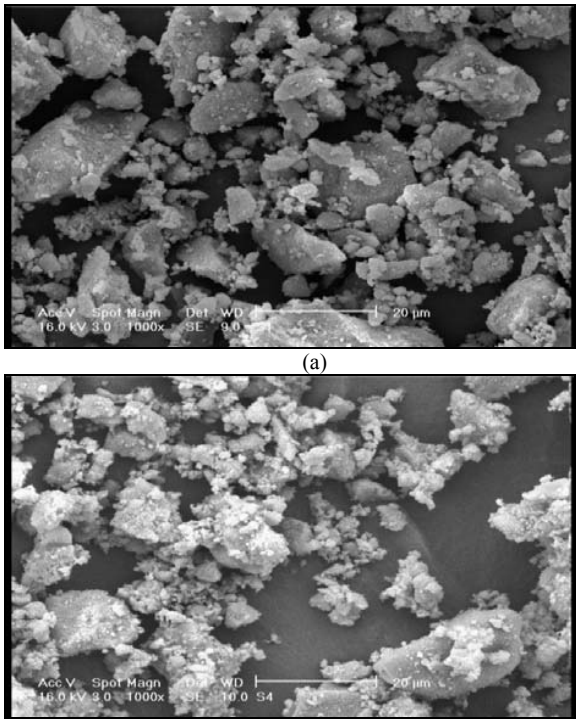


(a)



(b)

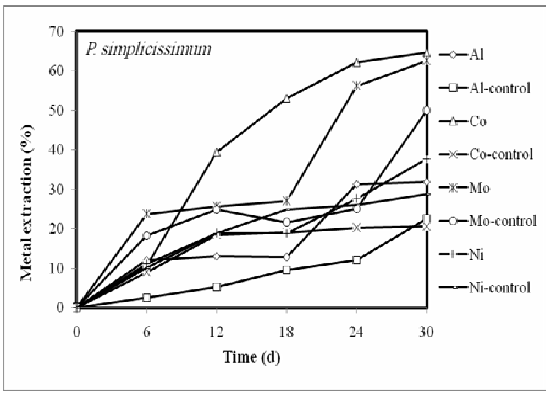
Fig. 1 SEM photomicrograph of the spent refinery catalyst (1000x magnification): (a) spent catalyst and (b) bioleached spent catalyst using A. niger after 30 days



(a)

(b)

Fig. 2 Variation of pH values in the one-step bioleaching process under optimum conditions using (a) A. niger and (b) P. simplicissmum



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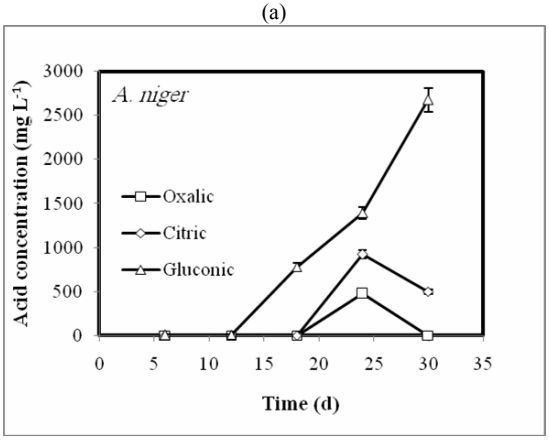
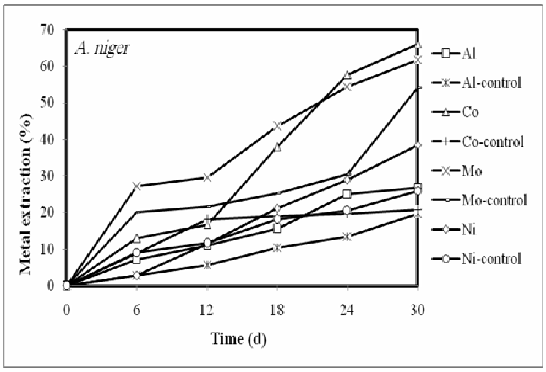
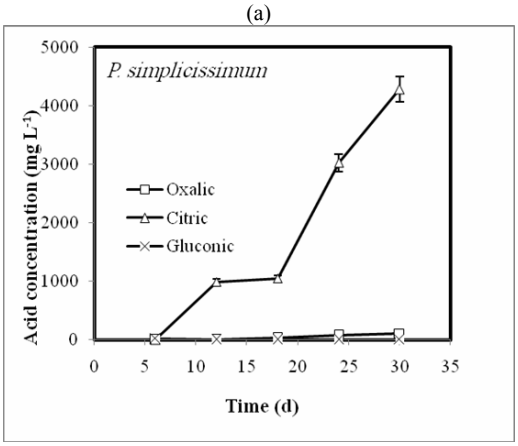


(b)

Fig. 3 Concentration of organic acids as a function of time in the one-step bioleaching process by (a) A. niger and (b) P. simplicissmum



(a)



(b)

Fig. 4 Percentage of extracted metal values from the spent catalyst using (a) A. niger and (b) P. simplicissmum strain during 30 days

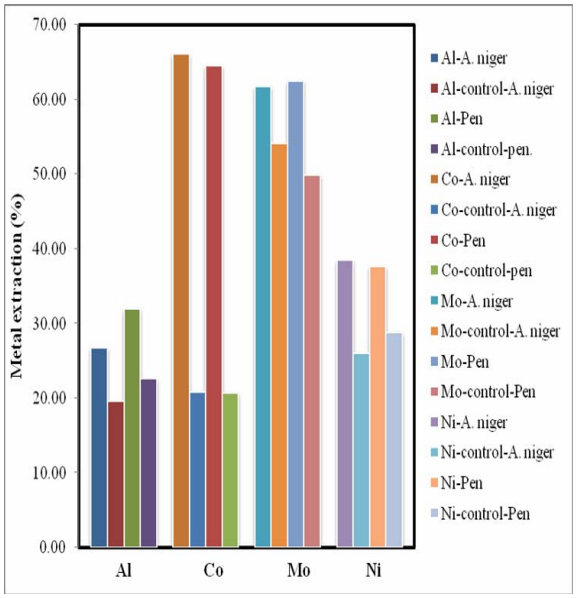


Fig. 5 Extraction yields of various metals from the spent catalyst under optimum bioleaching conditions by A. niger and P. simplicissimum

TABLE I
CHEMICAL COMPOSITION OF THE SPENT REFINERY CATALYST USING ICP-OES

Elements	Units	Spent catalyst	Elements	Units	Spent catalyst
Ag	**ppm**	**10**	**Nb**	**ppm**	**399**
Al	**%**	**39.4**	**Ni**	**ppm**	**598**
As	**ppm**	**41**	**P**	**%**	**< 0.1**
Ba	**ppm**	**17**	**Pb**	**ppm**	**< 20**
Be	**ppm**	**0.8**	**Rb**	**ppm**	**3.8**
Bi	**ppm**	**< 5**	**S**	**%**	**0.50**
Ca	**%**	**0.02**	**Sc**	**ppm**	**< 2**
Cd	**ppm**	**< 2**	**Se**	**ppm**	**22**
Ce	**ppm**	**9**	**Si**	**%**	**0.15**
Co	**ppm**	**24000**	**Sn**	**ppm**	**4.1**
Cr	**ppm**	**160**	**Sr**	**ppm**	**11**
Cu	**ppm**	**88**	**Te**	**ppm**	**< 5**
Fe	**%**	**0.48**	**Th**	**ppm**	**13**
Hf	**ppm**	**130**	**Ti**	**%**	**< 0.1**
K	**%**	**< 0.1**	**U**	**ppm**	**< 10**
La	**ppm**	**3.1**	**V**	**ppm**	**< 10**
Li	**ppm**	**< 1**	**W**	**ppm**	**18**
Mg	**%**	**< 0.1**	**Y**	**ppm**	**< 1**
Mn	**%**	**< 0.1**	**Yb**	**ppm**	**< 1**
Mo	**ppm**	**80000**	**Zn**	**ppm**	**110**
Na	**%**	**< 0.2**	**Zr**	**ppm**	**41**