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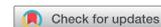
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Changes in the fractionation profile of Al, Ni, and Mo during bioleaching of spent hydroprocessing catalysts with *Acidithiobacillus ferrooxidans*

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ABSTRACT

Spent hydroprocessing catalysts are known to contain a variety of potentially toxic metals and therefore studies on the bioavailability and mobility of these metals are critical for understanding the possible environmental risks of the spent catalysts. This study evaluates the different chemical fractions/forms of aluminium (Al), nickel (Ni), and molybdenum (Mo) in spent hydroprocessing catalyst and the changes they undergo during bioleaching with *Acidithiobacillus ferrooxidans*. In the spent catalyst (prior to bioleaching), Al was primarily present in its residual form, suggesting its low environmental mobility. However, Ni comprised mainly an exchangeable fraction, indicating its high environmental mobility. Molybdenum was mainly in the oxidizable form (47.1%), which indicated that highly oxidizing conditions were required to liberate it from the spent catalyst. During bioleaching the exchangeable, reducible and oxidizable fractions of all the metals were leached, whereas the residual fractions remained largely unaffected. At the end of bioleaching process, the metals remaining in the bioleached sample were predominantly in the residual fraction (98.3–99.5%). The 'risk assessment code' (RAC) and I_R analysis also demonstrated that the environmental risks of the bioleached residue were significantly lower compared to the untreated spent catalyst. The results of this study suggest that bioleaching is an effective method in removing the metals from spent catalysts and the bioleached residue poses little environmental risk.

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Bioleaching; fractionation; metals; spent catalyst; environmental risk; reduced partition index

Introduction

Petroleum refineries worldwide generate between 170,000 and 200,000 tons of spent hydroprocessing catalysts every year.^[1] The U.S. Environmental Protection Agency considers spent hydroprocessing catalysts to be hazardous.^[2] Therefore, their safe disposal is a serious concern for petroleum refineries worldwide. Spent hydroprocessing catalysts contain valuable metals such as cobalt (Co), molybdenum (Mo), nickel (Ni), aluminum (Al), and vanadium (V).^[3] Therefore, spent catalysts may provide a rich secondary source for these metals.^[4] A sustainable spent catalyst management strategy requires the development of innovative recycling processes, which enable the recovery of valuable metals and ensures the safe disposal of spent hydroprocessing catalysts. Conventionally, recovery of metals from the spent refinery catalyst is achieved by either pyrometallurgical methods, hydrometallurgical methods, or a combination of both.^[5,6] Although these methods have been shown to have good extraction efficiencies, there are many disadvantages. For example, pyrometallurgical methods are highly energy intensive, require significant capital cost, and generate toxic gases. Similarly, hydrometallurgical processes require a large quantity of chemicals, expensive downstream processing, and produce secondary pollution.^[7] Therefore, the research focus has more recently shifted toward the

development of more sustainable, eco-friendly methods for the recovery of metals from spent catalysts.

In recent years, a biotechnological leaching technique called 'bioleaching' has gained attention as an efficient and eco-friendly method for the recovery of metals from spent catalysts.^[7] The bioleaching technique exploits the oxidation potential of acidophilic bacteria such as *Acidithiobacillus ferrooxidans* (*At. ferrooxidans*) and *Acidithiobacillus thiooxidans* (*At. thiooxidans*) to transform insoluble metallic species to soluble entities. Many studies have reported the potential of bioleaching in the recovery of different metals (Al, Mo, Ni, and V) from spent catalyst.^[7–9] In most of these studies, the bioleaching yield of the metal was reported based on the total metal content of individual metals. However, it is now widely recognized that determining the total content of metals does not adequately quantify their bioavailability and mobility, or their potential environmental risks.^[10] This is because toxicity depends not only on total concentrations but also on the bioavailable fraction of a given metal.^[11] The metals present in the spent catalyst are therefore likely to exist in different chemical fractions, which will eventually affect their mobility and bioavailability.^[8] In addition, the efficiency of the bioleaching process will also be largely dependent on the fractionation of metals, as each metal exhibits different energy states in the spent catalysts.

A fractionation study during bioleaching may provide useful insights on metals and the fractions, which are likely to be leached during bioleaching. The fractionation information of the bioleached residue will also determine whether it is safe to dispose of the bioleached spent catalysts. It was found that during bioleaching using *At. thiooxidans*, a sulfur-oxidizing microorganism, significant changes in the fractions of metals such as Al, Ni, V, and Mo occurred.^[12] Besides *At. thiooxidans*, another acidophile, *At. ferrooxidans*, is also capable of bioleaching metals from spent catalysts. *At. ferrooxidans* is the most dominant bacteria in bioleaching operations, and has the capacity to oxidize both ferrous iron (Fe^{2+}) and sulfur compounds into ferric (Fe^{3+}) and H_2SO_4 . The use of *At. ferrooxidans* during bioleaching of spent catalyst can be advantageous due to its ability to oxidize both reduced sulfur and iron compounds as opposed to sulfur only using *At. thiooxidans*. The bioproducted Fe^{3+} coupled with H_2SO_4 acts as a strong oxidant and may leach a variety of metallic sulfides and oxides in an acidic medium. Although many studies have reported the potential of *At. ferrooxidans* in leaching metals from spent catalysts, to date no study has investigated the changes in the fractionation of metals during bioleaching of spent catalyst using *At. ferrooxidans*. It is important to note that the use of *At. ferrooxidans* during bioleaching may impact the fractionation behavior of metals differently than what has been reported previously with *At. thiooxidans* due to the symbiotic action of Fe^{3+} and H_2SO_4 produced by the former.^[12] This study, therefore, aims to investigate this important aspect and quantify the fractionation profile of Al, Ni, and Mo in the spent catalysts and the changes they undergo during bioleaching. In addition, this study will evaluate the environmental risk of bioleached residue using the 'risk assessment code' (RAC) and 'reduced partition index' (I_R).

Materials and methods

Spent catalysts and characterization

The spent hydroprocessing catalysts used in this study, provided by a spent catalyst recycling company, were coated with carbon and were trilobular in the shape. They were dried at 105°C for 24 h, before being pulverized with a mortar and pestle. The spent catalysts were then digested with aqua regia ($\text{HCl} + \text{HNO}_3$, 3:1) (trace metal-free grade, Fisher Scientific, Loughborough, UK), and the digested liquid was filtered through Whatman No. 42 filter paper. The filtered, digested samples were transferred into trace metal-free centrifuge tubes (Labcon, Petaluma, CA, USA) and subjected to inductively coupled plasma mass spectroscopy (ICP-MS) (Perkin-Elmer ELAN DRC-e, USA) for the determination of Ni, Al, and Mo.^[13-14] The ICP-MS was calibrated using standards of Ni, Al, and Mo prepared from commercial stock solution (LGC, Standards, UK) and the accuracy of the results was checked by the inclusion of method blanks, duplicate samples and quality control standards (Inorganic Ventures, Lakewood, NJ, USA).

Spent catalysts were gold coated (Emitech K550, Quorum Technologies Ltd, West Sussex, United Kingdom) and subjected to scanning electron microscopy (SEM) in secondary electron mode using a Hitachi model S-4700 (Hitachinaka, Japan). The analyses were performed at an acceleration voltage

of 20 kv, an emission current (I_c) of $10 \mu\text{A}$ and a working distance of 12 mm.^[15] Energy dispersive spectrometry (EDS) [INCA[®]; Oxford Instruments (High Wycombe, UK)] in point and id mode was employed to estimate the % weight (Mean \pm S.D.) of the chemical elements present in spent catalysts.

Fractionation of metals in spent catalysts

The fractionation profile of metals (Al, Ni, and Mo) was investigated in the untreated spent catalysts (prior to bioleaching), during bioleaching, and in the bioleached residue using the sequential extraction procedure developed by the Community Bureau of Reference (BCR).^[16] The BCR process is a well-established and widely accepted sequential extraction process that has been successfully applied to study the fractionation of metals in spent catalyst, soil, sewage sludge, and river sediments.^[8, 17-20] In the BCR sequential extraction process, different fractions of metals are evaluated in four steps. The first step involves the extraction of the exchangeable fraction of metals, which are acid-soluble and/or bound to carbonate. This fraction represents the metals that are highly mobile and easily affected by the ionic composition of water. In the second step, the reducible fraction is extracted. The reducible fraction involves the extraction of metals bound to Fe-Mn oxide and which are susceptible to leaching in an acidic environment. In the third step, the oxidizable fraction is extracted, which represents the fraction of the metals bound to the organic matter and/or sulfide. The metals bound in this fraction require highly oxidizing conditions for their liberation from the matrix. The fourth step represents the residual fraction which are the most stable form of the metals. This fraction accounts for the metals that remain after extraction of the exchangeable, reducible and oxidizable fractions. The metals present in the residual fraction are incorporated in the crystal lattice of the mineral and do not release under normal environmental conditions.

To analyze the fractionation profile of metals, 0.250 g of spent hydroprocessing catalysts were placed in 50 mL polypropylene tubes. An appropriate volume of the prescribed extractants was added to spent catalyst and the extraction was performed.^[16, 21] The detail of the BCR sequential extraction scheme has been provided in Table 1. After completing the extraction step, the mixture was centrifuged at 8000 rpm for 20 min and the supernatant was filtered through Whatman No. 42 filter paper. The filtered supernatant was analyzed for metals content using ICP-MS. The residue was washed with distilled water, centrifuged, and the supernatant was discarded. After washing and centrifuging, the residue was subjected to the next extraction step. All analyses were conducted in duplicate.

Study on risk assessment code (RAC) and reduced partition index (I_R)

The reduced partition index (I_R) and risk assessment code (RAC) was employed to evaluate the environmental risks of the feed and bioleached spent catalyst. The I_R is a widely used method to quantify the relative binding intensity of a particular metal in different solid matrix.^[22] It also provides important information on the relative binding intensities of different metals in a particular matrix. The results of the BCR sequential

Table 1. BCR four-step sequential extraction procedure.

Si. No.	BCR Step	Extractable fraction	Extracting reagent	Conditions	Extracting period (hour)
i.	Step I	Exchangeable	40 mL of 0.11 mol ⁻¹ acetic acid (pH 3) for 1 g of sample	pH 3 (room temperature)	Shake at mechanical shaker for 16 h
ii.	Step II	Reducible	40 mL of 0.11 mol ⁻¹ hydroxylamine hydrochloride (pH 2)	pH 2 (room temperature)	Shake at mechanical shaker for 16 h
iii.	Step III	Oxidizable	20 mL 8.8 mol ⁻¹ hydrogen peroxide and 50 mL of 1 mol ⁻¹ ammonium acetate (pH 2)	Digestion with hydrogen peroxide at room temperature than at 80°C. Repeat the above step.	60 min at room temp. 60 min at 80°C.
iv.	Step IV	Residual	Remaining after above three steps		

extraction were used to analyse the I_R . The I_R is defined by:

$$I_R = \sum_{i=1}^k i^2 F_i / k^2$$

Where i indicates the index number of the BCR sequential extraction step, $k = 4$ (total steps in BCR sequential extraction), and F_i is the percentage of a particular metal in fraction i . As per BCR sequential extraction procedure, the minimum possible value of I_R can be 0.06 if the metal percentage in the exchangeable fraction is 100%. Similarly, the maximum I_R value is 1 where the percentage of the metal in the residual fraction is 100%. This indicates that any metal with an I_R value close to minimum (0.06) will exhibit very weak binding. Due to the weak binding, these metals will experience high mobility in the environment. On the other hand, metals with an I_R value close to 1 will experience strong binding. Such metals will be highly stable and won't release into the environment for a long time.

Similarly, RAC is a widely recognized tool to evaluate the bioavailability of metals in a solid matrix. The RAC in the feed and bioleached spent catalyst is the ratio of the amount of metal in the exchangeable fraction to the total concentration of a particular metal and is expressed by^[20]:

$$RAC = C_m / C_{total} \times 100$$

Where C_m is the metal concentration in the exchangeable fraction and C_{total} is the total concentration of a particular metal in the spent catalyst sample. As per RAC guidelines, any metal having <1% of its total content in the exchangeable fraction may be considered to be safe for the environment and poses no risk. Based on the exchangeable fraction content, the RAC can be postulated on the scale of 1% to 100%: <1% (no risk), 1% to 10% (low risk), 11% to 30% (medium risk), 31% to 50% (high risk), and >50% (very high risk) for a given metal.

Microorganisms and growth conditions

The microorganisms used in the current study were a pure bacterial culture of *At. ferrooxidans*. The microorganisms were grown in 0K basal media (pH 1.8) fortified with 4 g/L of ferrous iron (as FeSO₄·7H₂O). The composition of 0K media has been provided elsewhere.^[8] The batch culture of *At. ferrooxidans* was incubated in a rotary shaker at 30°C and 150 rpm. Ultra-pure water (18.3 mΩ, Milli-Q Element SystemTM, Merck

Millipore, USA), water and analytical grade chemicals were used to prepare all the solutions.

Bioleaching experiments

The bioleaching experiments were performed for 15 days in 1500 mL Erlenmeyer flasks, each with a 500 mL working volume. For bioleaching with *At. ferrooxidans*, a two-step process was applied. In the first step, grown cells of *At. ferrooxidans* were suspended in 500 mL fresh 0K medium. The 0K media was provided with 1% S⁰ (w/v) and 4 g/L Fe²⁺ (w/v) at an initial pH of 1.8. During this step, *At. ferrooxidans* completely oxidized the Fe²⁺ to Fe³⁺ and part of S⁰ to H₂SO₄. This led to a decrease in the pH of the medium to 1.5 from an initial pH of 1.8. This medium was filtered through Whatman filter paper No. 1 to remove the suspended sulfur particles. In the second step, the spent catalysts were added at 3% w/v to this medium (pH 1.5) having biological produced lixivants (Fe³⁺ and H₂SO₄) and bacterial cells. During bioleaching, the pH was monitored using a pH meter. An appropriate volume of the sample was withdrawn daily and filtered through Whatman No. 42 filters. After filtration, the spent catalyst retained on the filter paper was dried at 105°C and subjected to a fractionation study. The liquor containing dissolved metals was acidified using HNO₃ and analyzed for metal content using ICP-MS.

Results and discussions

Fractionation profile of Al, Ni, and Mo in the spent catalysts

The spent catalysts contained Al, Ni, and Mo concentrations of 96.5, 17.7, and 82.6 mg/g. The SEM-EDS analysis also confirmed the presence of these elements in the spent catalyst (Fig. 1A). The fractionation profile of the metals in the spent catalysts (before bioleaching) and in the bioleached residue are shown in Figs. 1B and 1C, respectively. A high proportion of Al was present in the residual fraction before bioleaching (64.8 mg/g; 67.1%) followed by the oxidizable fraction (13.7 mg/g; 14.2%). Metals present in the residual fraction are mainly bound into crystal lattice structures and are extremely difficult to release under normal environmental conditions.^[23] The presence of Al in this fraction therefore suggested that the potential mobility and solubility of Al was extremely low. The presence of Al in the residual fraction can be explained on the basis of its predominant presence as a stable oxide (Al₂O₃) in the spent hydroprocessing catalysts.^[24] The predominant

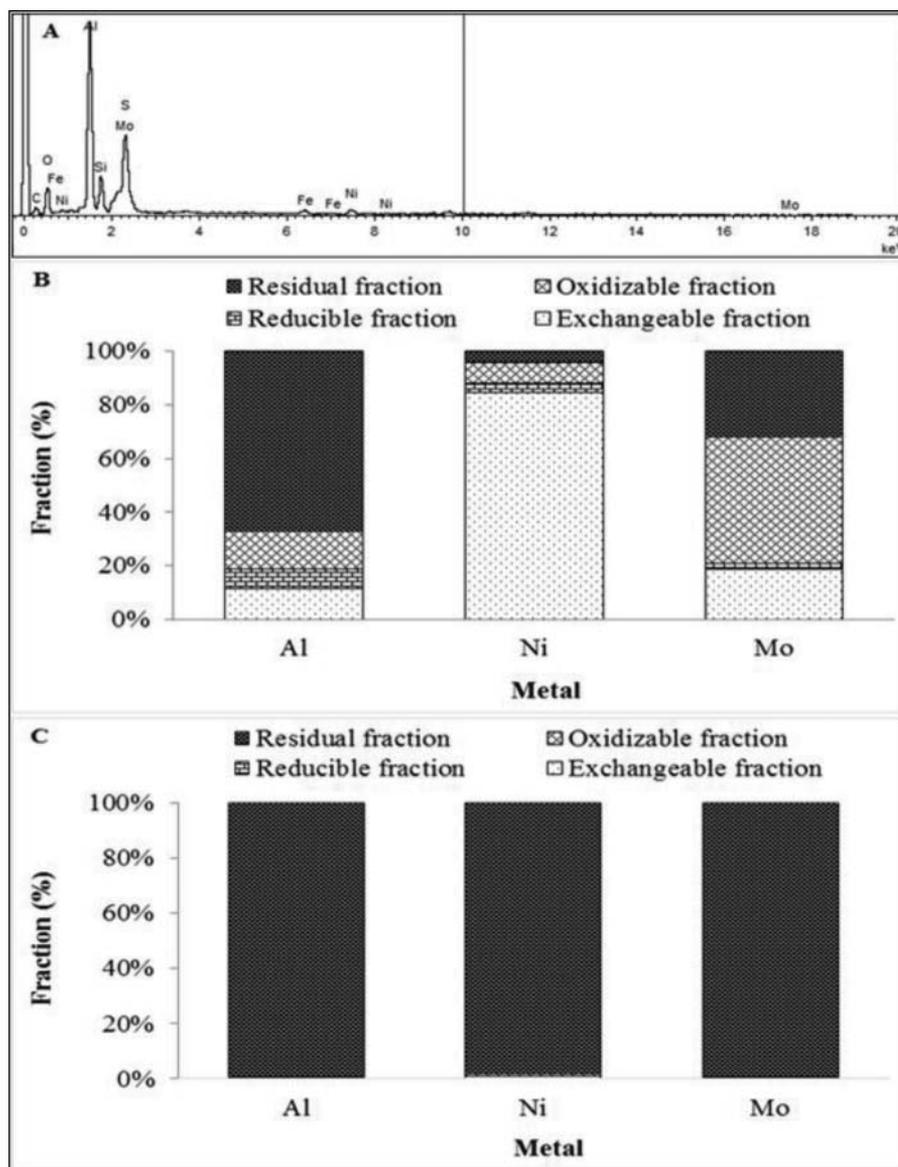


Figure 1. (A) SEM-EDX spectrum of the spent catalyst (B) fractionation of Al, Ni, and Mo in the untreated spent catalysts (before bioleaching) (C) fractionation of Al, Ni, and Mo in the bioleached, spent catalysts.

presence of Al in the residual fraction has been reported.^[12] However, in that study, a higher proportion of Al (83.9%) was present in the residual fraction compared to the current study (67.1%). The difference may be attributed to the fact that the spent catalysts originated from different petroleum refineries and had different chemical characteristics. In addition, in the above reported study, spent catalysts were deoiled using acetone.^[12] It is believed that during the process of deoiling, most of the oil is removed which increases the overall content of this fraction in the medium. In addition, the total content of Al (20.56%) in deoiled spent catalysts was also higher when compared to the current study (9.65%).

The fractionation profile of Ni in the untreated spent catalyst before bioleaching was different to that of Al. Nickel was predominantly present in the exchangeable fraction (14.9 mg/g), accounting for 84.7% of the total Ni present in the spent catalysts. As per the BCR scheme, the metals existing in the exchangeable fraction are easily soluble and have high mobility.

The predominant presence of Ni in exchangeable fraction therefore suggests that the potential mobility of Ni is very high and hence it may solubilize easily during bioleaching. The higher presence of Ni in the exchangeable fractions has been reported previously.^[12]

Among all the metals analyzed, the highest proportion of the oxidizable fraction before bioleaching was observed for Mo. The concentration of Mo in oxidizable fraction was about 38.9 mg/g, which accounted for 47.1% of the total Mo in spent catalysts. This was followed by the residual fraction (26.5 mg/g). The relatively higher proportion of Mo in the oxidizable fraction suggests that either Mo is bound with organic matter or is present as a sulfide in the spent catalysts. The presence of Mo in the oxidizable fraction was expected, as Mo tends to exist as MoS_2 in hydroprocessing catalysts.^[25] In addition, the tendency of Mo to associate with the organic matter in the solid matrices has been reported in other studies.^[26-27] The presence of Mo in the oxidizing fraction indicates that strong oxidizing

conditions are required in order to leach it from spent hydro-processing catalysts. Moreover, an appreciable concentration of Mo was also present in the residual fraction (32.1%), which indicated that part of the Mo may remain stable for a long period and therefore, will be difficult to liberate from spent catalysts.

Variations in pH and leaching yields of Al, Ni, and Mo during bioleaching

The pH initially increased slightly from a value of 1.5 to 1.9 on the 3rd day of the experiment (results not displayed). However, there was no further increase in the pH. The increase in pH during bioleaching was due to the reaction of metallic oxides and sulfides with protons. The increase in medium pH during bioleaching of spent catalysts has been reported elsewhere.^[28]

Among all the metals, the bioleaching yield of the Ni was highest (Fig. 2) and was almost complete by the 3rd day of the bioleaching experiment. A slight decrease in the leaching yield of Ni was observed at the end of bioleaching, which may have been due to the re-adsorption of the Ni on the spent catalyst's surface. The high yield of Ni during bioleaching may be attributed to its presence mainly in the exchangeable fraction of the spent catalyst. The high leaching yield of Ni has been reported in many bioleaching studies conducted with spent catalyst.^[12,28] Dissimilar to Ni, 32.8% of the Al was bioleached from the spent catalysts by the 3rd day of bioleaching, and increased gradually to 36.9% by the end of the experiment. The low leaching yield of Al during bioleaching was expected, as the large quantity of Al (67.1%) was present in the residual fraction of the spent catalysts. The low bioleaching yield of Al during bioleaching has been reported in other studies.^[12, 29] The initial leaching yield of Mo was low by the end of the experiment, as 46.3% of the total Mo was leached. The lower leaching yield of Mo, compared to Ni, was due to its presence mainly in the oxidizable (47.1%) and residual fraction (32.1%) of the spent catalysts. The lower leaching yield of Mo was also reported in other bioleaching studies.^[25]

Changes in fractionation of Al, Ni, and Mo during bioleaching with *At. ferrooxidans*

Changes in fractionation profile of Al

The results of changes in fractionation profile of Al during bioleaching are presented in Fig. 3A. At the start of bioleaching, 64.8 mg/g of Al (67.1% of the total Al) was present in the residual fraction. The second largest fraction of Al in the spent

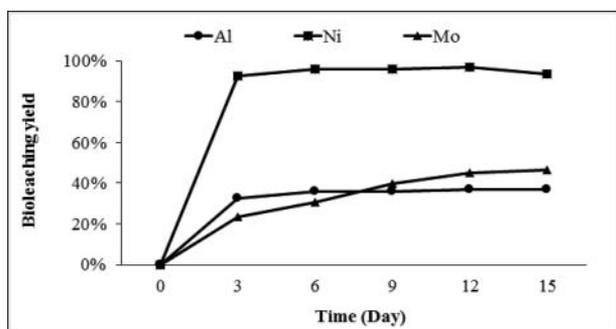


Figure 2. Bioleaching yield of Al, Ni, and Mo.

catalyst was in the oxidizable fraction (13.7 mg/g), which was followed by the exchangeable fraction (11.3 mg/g). During bioleaching, the exchangeable fraction of Al decreased to 0.13 mg/g within first 3 days of bioleaching, and continued to decrease slowly until the end of the study. The decrease (99.2%) in this fraction was expected, as it is considered to be a highly reactive fraction that leaches rapidly under the acidic conditions of bioleaching. Pathak et al. (2014) also found that during bioleaching of deoiled spent catalyst with *At. thiooxidans*, the leaching of the exchangeable fraction of Al was rapid and about 83% of the exchangeable fraction was leached within the first 24 h of bioleaching.^[12]

At the start of bioleaching, the reducible fraction was 6.7 mg/g, which also decreased rapidly over the duration of the experiment. The significant removal of this fraction may also be explained by the acidic conditions during bioleaching, which caused removal of this fraction. As per the BCR scheme, the metals present in the reducible fraction are those which are trapped by Fe oxides. These Fe-oxides act as a scavenger for metals and can be easily mobilized under acidic conditions.^[30]

Similar to the exchangeable and reducible fractions, a rapid decrease in the oxidizable fraction of the Al was observed during bioleaching. The decrease in this fraction (98.8%) was significantly higher compared to a previous study,^[12] which measured a decrease of 11%. This difference may be explained by the fact that the above reported study was conducted with *At. thiooxidans*, whereas the current study was conducted with *At. ferrooxidans*, which produced Fe^{3+} in the leaching media. The Fe^{3+} acts as a strong oxidant which can oxidize the insoluble metal sulfides into metallic sulfate, leading to the leaching of oxidizable fraction of Al. The role of Fe^{3+} in potential dissolution of metallic sulfide/organic bound metal was also confirmed in a study conducted with contaminated dredged sediments.^[31] In addition, the concentration of oxidizable fraction of Al was lower in the current study (6.9%) compared to the previous reported study (9%), so more leaching agents (lixiviants) were available to react with the sulfide fraction of the Al.^[12] As the oxidizable fraction represents the metals that are mostly present as sulfides, a higher decrease in this fraction was observed in the current study. In addition, the chemical characteristics of the spent catalyst were different in the previously reported study,^[12] where it contained high concentrations of V (11.4%), whereas the spent catalysts used in the current study had no V and mainly contained Al, Ni, and Mo.

Among all fractions, the residual fraction of Al had the lowest decrease. This was due to the fact that the metals associated with the residual fraction are thermodynamically stable and exhibit little mobility. Prolonged acidic conditions, coupled with a highly oxidizing environment, are required to release these metals from the matrix. A previous bioleaching study conducted with contaminated sediment also confirmed that during bioleaching most of the mobile fraction of the metals were leached, whereas the residual fraction of the metals remained largely unchanged.^[32]

Changes in fractionation profile of Ni

At the start of bioleaching, a large quantity of the Ni (14.9 mg/g) was present in the exchangeable fraction. During bioleaching, almost complete removal (99.8%) of the

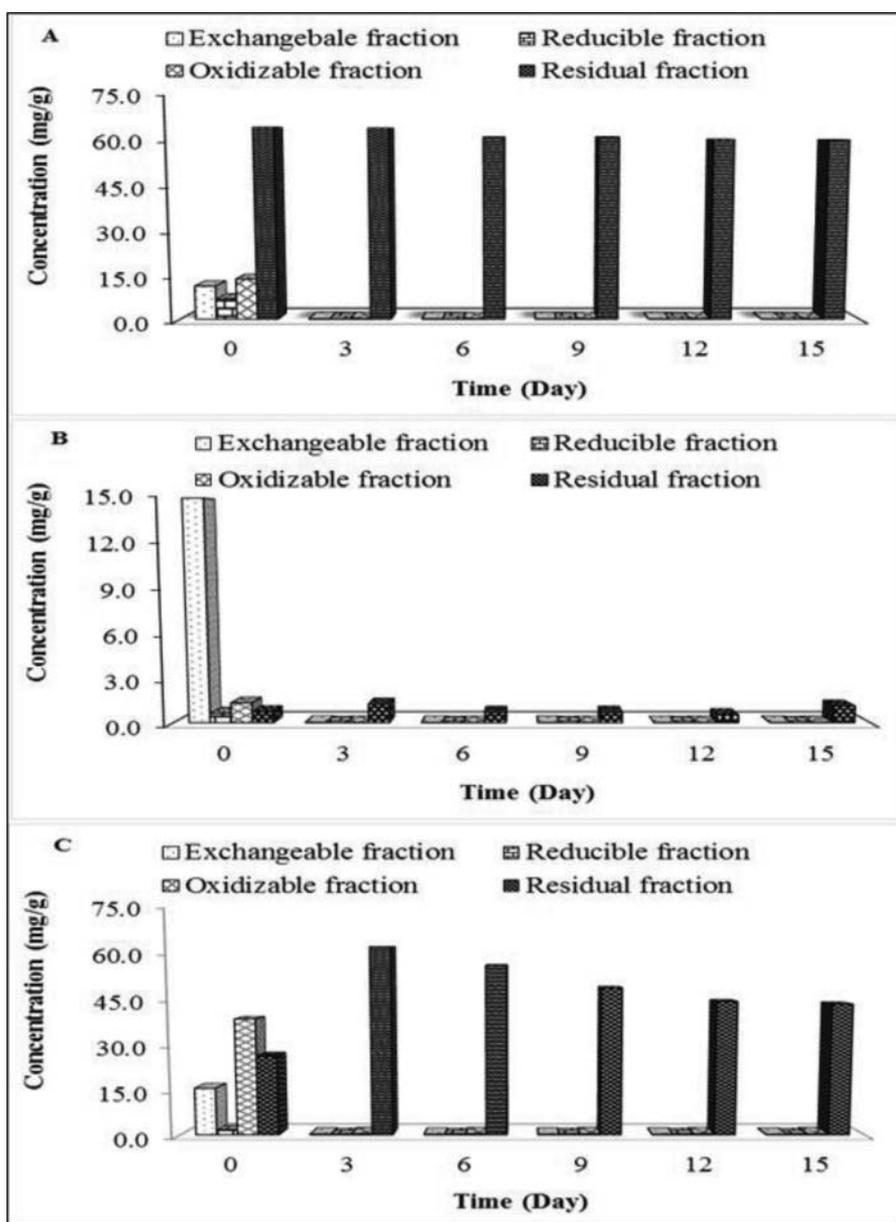


Figure 3. (A) Fractionation behavior of Al during bioleaching (B) fractionation behavior of Ni during bioleaching (C) fractionation behavior of Mo during bioleaching.

exchangeable fraction took place (Fig. 3B). At the end of bioleaching, an almost negligible amount (0.012 mg/g) of the exchangeable fraction remained in the spent catalysts. The large decrease in this fraction can be explained by the fact that the metals present in the exchangeable fraction are highly mobile and may be leached rapidly during bioleaching. A similar leaching pattern of the exchangeable fraction of the Ni had been reported in our previous study, where about 97% of the exchangeable fraction of Ni was leached within first day of bioleaching.^[12] Similar to exchangeable fraction, almost complete removal (98.8%) of the reducible fraction was observed during bioleaching. A similar leaching pattern was observed for the oxidizable fraction. The decrease in this fraction was significantly higher than reported (71.43%) in the previous study using *At. thiooxidans*.^[12] Moreover, a similar higher leaching of the oxidizable fraction had been observed for Al. The higher leaching of oxidizable fraction of the Ni can be similarly explained

by the presence of bio-produced Fe^{3+} in the leaching media. The bio-produced Fe^{3+} is an oxidant, which has the potential to chemically oxidize the insoluble metal sulfides into metallic sulfate. In addition, the bacteria itself can oxidize the metallic sulfides into readily soluble metallic sulfates. As the oxidizable fraction mainly consists of the metal portion which is bound either to organics or sulfide, the possible oxidation of metal sulfides led to the larger decrease in this fraction. In the case of the residual fraction, no decrease was observed during bioleaching. The relatively low leaching of residual fraction of the different metals has been reported in various bioleaching studies conducted with sediments.^[12, 33-34]

Changes in fractionation profile of Mo

The fractionation profile of Mo during bioleaching is shown in Fig. 3C. Prior to bioleaching, Mo mainly existed in the oxidizable fraction (38.9 mg/g), followed by residual (26.5 mg/g),

exchangeable (15.7 mg/g), and reducible fractions (1.5 mg/g). Similar to Al and Ni, the exchangeable, reducible and oxidizable fractions of the Mo were quickly bioleached. The residual fraction increased to 62.7 mg/g on the third day of bioleaching from an initial value of 26.5 mg/g. After this initial increase, there was a gradual decrease in the residual fraction. The exact reason for the increase in the residual fraction of Mo is not clear. However, it may be speculated that the bioleaching transformed a large portion of oxidizable and/or exchangeable fraction into the residual fraction. During bioleaching, the leached Mo from the spent catalyst may have been precipitated and bound to crystalline alumina as aluminum molybdate. This may have increased to the overall residual fraction. The tendency of Mo to precipitate as MoO_3 during bioleaching has been reported.^[25] Moreover, at the start of bioleaching, a large amount (4000 mg/L) of bioproducted Fe^{3+} was in the media which may have also led to the precipitation of Mo as insoluble ferric molybdate.^[35] During bioleaching, minor depositions of ferric precipitates on the glassware were observed. These findings indicated that the leaching of a metal during bioleaching was highly related with its fractionation.

Fractionation profile of metals in the bioleach spent catalysts

Although bioleaching with *At. ferrooxidans* resulted in significant leaching of Al, Ni and Mo from spent catalysts, a significant quantity of these metals (63.1% of Al, 6.5% of Ni, and 53.7% of Mo) still remained in the bioleached spent catalysts. The remaining metals present in the bioleached spent catalysts are likely to exist in different fractions that will govern the ultimate fate of the spent catalyst for its safe disposal. It was found that bioleaching affects the distribution fractions of all metals present in the bioleached spent catalysts. The results indicated (Fig. 1b) that the metals remaining in the bioleached spent catalysts were predominantly in the residual fraction (98.3–99.5%) and therefore were likely to have low environmental mobility. In bioleached spent catalysts, 99.5% Al, 98.3% Ni, and 98.9% Mo existed in the residual fraction. Previous bioleaching studies conducted with spent catalyst, mine tailing and soil also confirmed that after bioleaching, most of the metals remained in the stable fraction.^[12, 34, 36]

RAC and I_R

The results of the show study show that the environmental risk of the spent catalysts based on the RAC for Al (exchangeable fraction is 11.7%) and Mo (exchangeable fraction is 19.0%) was 'medium', but was 'very high' for Ni (Fig. 4). After bioleaching, the RAC value decreased, along with the environmental risk of these metals. In the bioleached spent catalyst, the Al (exchangeable fraction of 0.1%) and Mo (exchangeable fraction of 0.3%) were in the 'no risk' category, whereas Ni (exchangeable fraction of 1.0%) posed only 'low risk'.

In the case of I_R , the relative binding intensity of each metal was different in the spent catalysts. The values of I_R for untreated and bioleached spent catalyst are presented in Fig. 5. In the spent catalyst, the lowest I_R value (0.15) was

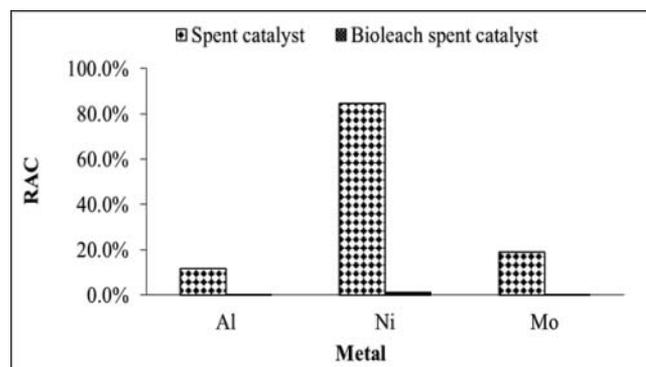


Figure 4. RAC values of the metals in the untreated and bioleach spent catalyst.

observed for Ni, whereas Al exhibited the highest value (0.78). The Mo had an intermediate value (0.60). The low I_R value of Ni was due to its high presence in the exchangeable fraction, which indicated its higher bioavailability. On the contrary, the high I_R value of Al was largely due to its presence mainly in the residual fraction. The high I_R value of Al indicated that binding of Al in the spent catalyst was strong and therefore may not be mobile in the environment. Due to bioleaching, significant changes in the binding intensity of metals in the bioleached spent catalyst were observed. The changes in I_R value of the metal were mainly caused by the removal of non-residual fractions (exchangeable, reducible, and oxidizable). In the bioleached spent catalysts, the I_R value for each metal was higher compared to the feed spent catalysts (Fig. 5). The I_R value of Al increased from 0.78 in the spent catalyst to 1.0 in the bioleached spent catalysts. Similarly, the I_R value of Mo increased from 0.60 in the spent catalysts to 0.99 in the bioleached spent catalysts. The most striking increase was observed for the Ni, for which the I_R value increased to 0.99 in the bioleached spent catalyst compared to 0.15 in the spent catalysts. The I_R results suggested that bioleaching led to a significant increase in the binding intensity of the metals present in the bioleached spent catalysts. The increase in the binding intensity of the metals was largely due to the leaching of mobile fractions and an overall increase in the residual fraction. As a result, the metals present in the bioleached spent catalysts experienced high binding intensities (0.99–1.0) and were therefore highly stable.

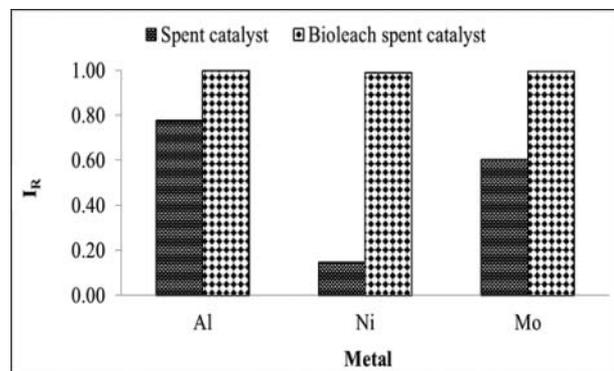


Figure 5. I_R values of the metals in the untreated and bioleach spent catalyst.

Conclusions

The results of the current study show that spent hydroprocessing catalysts contain different metals (Al, Ni, and Mo) which exhibit different mobility and bioavailability and poses significant environmental risk. Bioleaching using *At. ferrooxidans* was highly effective in the removal of these metals from the spent catalyst. Moreover, during bioleaching the removal of non-residual fractions (exchangeable, reducible, and oxidizable) of all the metals was observed, whereas the residual fraction of the metals was largely unaffected. Due to the removal of non-residual fractions, the binding intensities of all the metals increased, whereas the environmental risks decreased. The results of the current study are useful in the development of a suitable bioleaching strategy for decontamination of hazardous spent hydroprocessing catalysts.

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References

- Marafi, M.; Stainslaus, A.; Furimsky, E. *Handbook of spent hydroprocessing catalyst*, Elsevier: The Netherlands, 2010.
- USEPA (United State Environmental Protection Agency). Hazardous Waste Management System. *Federal Register* **2003**, 68(202), 59935–59940.
- Pathak, A.; Srichandan, H.; Kim, D. J. 2015. Feasibility of Bioleaching in Removing Metals (Al, Ni, V and Mo) from as Received Raw Petroleum Spent Refinery Catalyst: A Comparative Study on Leaching Yields, Risk Assessment Code and Reduced Partition Index. *Mate. Trans.* **2015**, 56(8), 1278–1286. DOI: 10.2320/matertrans.M2015104.
- Akcil, A.; Veglio, F.; Ferella, F.; Okudan, M. D.; Tuncuk, A. 2015. A Review of Metal Recovery from Spent Petroleum Catalysts and Ash. *Waste Manage.* **2015**, 45, 420–433. DOI: 10.1016/j.wasman.2015.07.007.
- Parhi, P. K.; Park, K. H.; Senanayake, G. A Kinetic Study on Hydrochloric Acid Leaching of Nickel from Ni–Al₂O₃ Spent Catalyst. *J. Ind. Engg. Chem.* **2013**, 19(2), 589–594. DOI: 10.1016/j.jiec.2012.09.028.
- Pinto, I.S.S.; Sadeghi, S. M.; Izatt, N. E.; Soares, H.M.V.M. 2015. Recovery of Metals from an Acid Leachate of Spent Hydrodesulphurization Catalyst using Molecular Recognition Technology. *Chem. Engg. Sci.* **2015**, 138, 353–362. DOI: 10.1016/j.ces.2015.08.018.
- Asghari, I.; Mousavi, S. M.; Amiri, F.; Tavassoli. 2013. Bioleaching of Spent Refinery Catalysts: A Review. *J. Ind. Engg. Chem.* **2013**, 19(4), 1069–1081. DOI: 10.1016/j.jiec.2012.12.005.
- Srichandan, H.; Pathak, A.; Singh, S.; Blight, K.; Kim, D. J.; Lee, S. W. Sequential Leaching of Metals from Spent Refinery Catalyst in Bioleaching–Bioleaching and Bioleaching–Chemical Leaching Reactor: Comparative Study. *Hydrometallurgy.* **2014**, 150, 130–143. DOI: 10.1016/j.hydromet.2014.09.019.
- Vyas, S.; Ting, Y.P. Sequential Biological Process for Molybdenum Extraction from Hydrodesulphurization Spent Catalyst. *Chemosphere.* **2016**, 160, 7–12. DOI: 10.1016/j.chemosphere.2016.06.060.
- Nunes, J. R.; Miras, J. R.; Pineiro, A. L.; Loures, L.; Gil, C.; Coelho, J.; Loures, A. Concentrations of Available Heavy Metals in Mediterranean Agricultural Soils and Their Relation with Some Soil Selected Properties: A Case Study in Typical Mediterranean Soils. *Sustainability* **2014**, 6(12), 9124–9138. DOI: 10.3390/su6129124.
- Bondareva, L.; Teisserenc, R.; Pakharkova, N.; Shubin, A.; Dantec, T. L.; Renon, L.; Svoboda, I. Assessment of the Bioavailability of Cu, Pb, and Zn Through *Petunia Axillaris* in Contaminated Soils. *Int. J. Ecol.* **2014**, 2014, 1–6. DOI: 10.1155/2014/378642.
- Pathak, A.; Srichandan, H.; Kim, D. J. Fractionation Behavior of Metals (Al, Ni, V and Mo) during Bioleaching and Chemical Leaching of Spent Petroleum Refinery Catalyst. *Wat. Air Soil Poll.* **2014**, 225 (1893), 1–10.
- Ratcliff, J. J.; Wan, A.H.L.; Edwards, M. D.; Soler-Vila, A.; Johnson, M. P.; Abreu, M.H.; Morrison, L. Metal Content of Kelp (*Laminaria Digitata*) Co-Cultivated with Atlantic Salmon in an Intergrated Multi-Trophic Aquaculture System. *Aquaculture* **2015**, 450, 234–243. DOI: 10.1016/j.aquaculture.2015.07.032.
- Healy, M. G.; Ryan, P. C.; Fenton, O.; Peyton, D. P.; Wall, D.P.; Morrison, L. Bioaccumulation of Metals in Rye Grass (*Lolium Perenne* L.) following the Application of Lime Stabilised, Thermally Dried and Anaerobically Digested Sewage Sludge. *Eco. Environ. Safety.* **2016**, 130, 303–309. DOI: 10.1016/j.ecoenv.2016.04.026.
- Morrison, L.; Feely, M.; Stengel, D. B.; Blamey, N.; Dockery, P.; Sherlock, A.; Timmins, E. Seaweed Attachment to Bedrock: Biophysical Evidence for a New Geophycology Paradigm. *Geobiology.* **2009**, 7, 477–487. DOI: 10.1111/j.1472-4669.2009.00206.x.
- Ure, A. M.; Quevauviller, P. H.; Muntau, H.; Griepink, B. Speciation of Heavy Metals in Soils and Sediments. An Account of the Improvement and Harmonization of Extraction Techniques Undertaken under the Auspices of the BCR of the Commission of European Communities. *Int. J. Environ. Anal. Chem.* **1993**, 51, 135–151. DOI: 10.1080/03067319308027619.
- Calvino, D. F.; Barreiro, L. C.; Nunez, R. P.; Munoz, J.C.N.; Sanjurjo, M.J. F.; Rodriguez, E. A.; Delgado, A. N.; Estevez, M. A. Heavy Metals Fractionation and Desorption in Pine Bark Amended Mine Soils. *J. Environ. Manage.* **2017**, 192, 79–88. DOI: 10.1016/j.jenvman.2017.01.042.
- Fuentes, A.; Llorens, M.; Saez, J.; Soler, A.; Aguilar, M.; Ortuno, F. 2004. Phytotoxicity and Heavy Metals Speciation of Stabilized Sewage Sludges. *J. Haz. Mate.* **2004**, 108, 161–169. DOI: 10.1016/j.jhazmat.2004.02.014.
- Ignatowicz, K. The Impact of Sewage Sludge Treatment on the Content of Selected Heavy Metals and Their Fractions. *Environ. Res.* **2017**, 156, 19–22. DOI: 10.1016/j.envres.2017.02.035.
- Pejman, A.; Bidhendi, G. N.; Ardestani, M.; Saeedi, M.; Baghvand, A. Fractionation of Heavy Metals in Sediments and Assessment of Their Availability Risk: A Case Study in the Northwestern of Persian Gulf. *Marine Pollu. Bull.* **2017**, 114(2), 881–887. DOI: 10.1016/j.marpolbul.2016.11.021.
- Quevauvillcr, P.; Raurct, G.; Muntau, H.; Ure, A. M.; Rubio, R.; Lopez-Sannchez, J. F.; Fiedler, H. D.; Griepink, B. Evaluation of a Sequential Extraction Procedure for the Determination of Extractable Trace Metal Contents in Sediments. *Fresenius J. Anal. Chem.* **1994**, 349, 808–814. DOI: 10.1007/BF00323110.
- Miretzky, P.; Avendano, M. R.; Munoz, C.; Carrillo-Chavez, A. Use of Partition and Redistribution Indexes for Heavy Metal Soil Distribution after Contamination with a Multi-Element Solution. *J. Soils Sedim.* **2011**, 11(4), 619–627. DOI: 10.1007/s11368-011-0343-6.
- Olafisoye, B. O.; Oguntibeju, O. O.; Osibote, O. A. An Assessment of the Bioavailability of Metals in Soils on Oil Palm Plantations in Nigeria. *Pol. J. Environ. Stud.* **2016**, 25(3), 1125–1140. DOI: 10.15244/pjoes/60858.
- Marafi, M.; Rana, M. Refinery Waste: The Spent Hydroprocessing Catalyst and its Recycling Options. *WIT Trans. Ecol. Environ.* **2016**, 202, 219–230.
- Mishra, D.; Kim, D. J.; Ralph, D. E.; Ahn, J. G.; Rhee, Y.H. Bioleaching of Vanadium Rich Spent Refinery Catalysts Using Sulfur-Oxidizing Lithotrophs. *Hydrometallurgy.* **2007**, 88, 202–209. DOI: 10.1016/j.hydromet.2007.05.007.
- Wichard, T.; Mishra, B.; Myneni, S.C.B.; Bellenger, J. P.; Kraepiel, A. M.L. Storage and Bioavailability of Molybdenum in Soils Increased by Organic Matter Complexation. *Nat. Geosci.* **2009**, 2, 625–629. DOI: 10.1038/ngeo589.
- Zemberyova, M.; Hagarovaa, I.; Zimovaa, J.; Bartekovaa, J.; Kussb, H. M. Determination of Molybdenum in Extracts of Soil and Sewage

- Sludge CRMs After Fractionation by Means of BCR Modified Sequential Extraction Procedure. *Talanta*. **2010**, 82(2), 582–586. DOI: 10.1016/j.talanta.2010.05.010.
- [28] Bharadwaj, A.; Ting, Y. P. Bioleaching of Spent Hydrotreating Catalyst by Acidophilic Thermophile *Acidianus Brierleyi*: Leaching Mechanism and Effect of Decoking. *Bioresour. Technol.* **2013**, 130, 673–680. DOI: 10.1016/j.biortech.2012.12.047.
- [29] Mishra, D.; Ahn, J. G.; Kim, D. J.; Chaudhary, G. R.; Ralph, D. E. Dissolution Kinetics of Spent Petroleum Catalyst using Sulfur-Oxidizing Acidophilic Microorganisms. *J. Haz. Mater.* **2009**, 167, 1231–1236. DOI: 10.1016/j.jhazmat.2009.01.056.
- [30] Wali, A.; Colinet, G.; Ksibi, M. Speciation of Heavy Metals by Modified BCR Sequential Extraction in Soils Contaminated by Phosphogypsum in Sfax, Tunisia. *Environ. Res. Eng. Manage.* **2014**, 4(70), 14–26.
- [31] Fang, D.; Zhao, L.; Yang, Z. Q.; Shan, H. X.; Gao, Y.; Yang, Q. Effect of Sulphur Concentration on Bioleaching of Heavy Metals from Contaminated Dredged Sediments. *Environ. Technol.* **2009**, 30(12), 1241–1248. DOI: 10.1080/09593330903045115.
- [32] Zhu, J. Y.; Zhang, J. X.; Li, Q.; Han, T.; Hu, Y. H.; Liu, X. D.; Qin, W. Q.; Chai, Li; Qiu, G.Z. Bioleaching of Heavy Metals from Contaminated Alkaline Sediment by Auto- and Heterotrophic Bacteria in Stirred Tank Reactor. *Trans. Non-ferrous Metall.Soc. China*. **2014**, 24, 2969–2975. DOI: 10.1016/S1003-6326(14)63433-6.
- [33] Zeng, X.; Wei, S.; Sun, L.; Jacques, D. A.; Tang, J.; Lian, M.; Ji, Z.; Wang, J.; Zhu, J.; Xu, Z. Bioleaching of Heavy Metals from Contaminated Sediments by the *Aspergillus Niger* Strain SY1. *J. Soils Sedim.* **2015**, 15, 1029–1038. DOI: 10.1007/s11368-015-1076-8.
- [34] Kumar, N.; Nagendran, R. Fractionation Behavior of Heavy Metals in Soil During Bioleaching with *Acidithiobacillus Thiooxidans*. *J. Haz. Mater.* **2009**, 169(1-3), 1119–1126. DOI: 10.1016/j.jhazmat.2009.04.069.
- [35] Gupta, C. K. *Extractive metallurgy of molybdenum*, CRC Press: Routledge, **2017**.
- [36] Liu, Y. G.; Zhou, M.; Zeng, G. M.; Wang, X.; Li, X.; Fan, T.; Xu, W. H. Bioleaching of Heavy Metals from Mine Tailings by Indigenous Sulfur-Oxidizing Bacteria: Effects of Substrate Concentration. *Bioresour. Technol.* **2008**, 99, 4124–4129. DOI: 10.1016/j.biortech.2007.08.064.