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# Comparison of Bioleaching Process Between Two Fungi on Hazardous Heavy Metals Recovery from Spent Oil Refinery Catalysts

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# Introduction

- Spent catalysts contribute significantly to the amounts of solid wastes generated in the petrochemical industry
- The catalysts have a definite shelf life and deactivate with time; in fact, they often require replacement after two to three years of operation
- 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

# Introduction

- **Bioleaching:** ability of microorganisms (bacteria/fungi) to transform solid compounds to soluble and extractable elements that can be recovered.
- **Microorgansims:** *A. ferrooxidans & A. thiooxidans; A. niger & P. simplicissimum*
- **Mecchanisms:** **acidolysis**, comlexolysis, redoxolysis and bioaccumulation
- **Fungal leaching advantages:**
  - ability to grow under higher pH (favors the bioleaching of alkaline solid wastes
  - faster leaching process with a shorter lag phase
  - ability of excreted metabolites to form complexes with metal ions, thus reducing the toxicity of the metabolites to the biomass
- **Spent catalyst:** amounts of solid wastes generated in petrochemical industry (hydroprocessing, reforming, desulfurization)

# Objective:

- *A. niger* and *P. simplicissimum* were adapted to a mixture of Al, Co, Mo and Ni (at 100-800 mg/L)

- Growth of the adapted fungi in the presence of spent catalyst was monitored along with the <u>extracted metals</u> and the <u>organic acids</u> excreted during fungal leaching.

# Materials & methods:

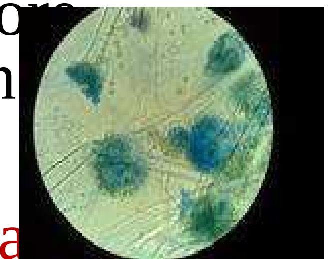
- **Spent catalyst:**
- **UOP: S-12 $Co/Mo/Al_2O_3$** (from naphtha treater unit), provided by one of the oil refineries in Iran.

- ✓ Extrudate in shape
- ✓ ~ 1.2 mm in diameter
- ✓ Surface area of 210 $m^2/g$
- ✓ pore volume of 0.5 $cm^3/g$

# Materials & methods:


➢ **Fungal strains and growth conditions:**

❖ *Aspergillus niger & Penicillium simplicissimum* obtained from NUS (National university of Singapo
Institute of Chemical and Biomolecular Engineerin



- ✓ Cultivated on 3.9% (w/v) potato dextrose aga
Dickinson, USA) plates
- ✓ Kept in an incubator for 7 days at 30 °C
- ✓ The number of spores was counted under an optical microscope (Olympus BH-2) at 400× magnification
- ✓ spore suspension was diluted with deionized water to the concentration of $10^7$ spores/mL
- ✓ pH of the solution was measured using a pH meter (pH lab, model 827) at regular time intervals.

# Materials & methods:

- **Bioleaching experiments:**
  - ✓ adding 1 mL of spore suspension into 500 mL Erlenmeyer flask containing 100 mL of sucrose medium (Merck)
  - ✓ Period of 30 days, under optimized values of pH, T, pulp density, inoculation percent and rotation speed.
- **Media for growing the fungi:**

| Material | Value |
| --- | --- |
| **Sucrose** | **100 g/L** |
| **$NaNO_3$** | **1.5 g/L** |
| **$KH_2PO_4$** | **0.5 g/L** |
| **$MgSO_4.7H_2O$** | **0.025 g/L** |
| **KCl** | **0.025 g/L** |
| **yeast extract** | **1.6 g/L** |

- **Control:** deionized water + sucrose medium + spent catalyst

# Analytical methods:

- **HPLC analysis** (HP1100 series) with UV (210 nm) and RI detectors, conducted by the Iran Mineral Processing Research Center (IMPRC)

✓ for organic acids produced

- **Analysis of metal composition:**

✓ By ICP-OES after acid digestion of the samples. Inductive Coupled Plasma-Optical Emission Spectrometry

# Results & discussion

- Characterization of the spent refinery processing catalyst by ICP-OES:

✓ Al (39.4%)

✓ Co (2.4%)

✓ Mo (8%)

✓ Ni (0.06%)

# Characterization of the spent catalyst:

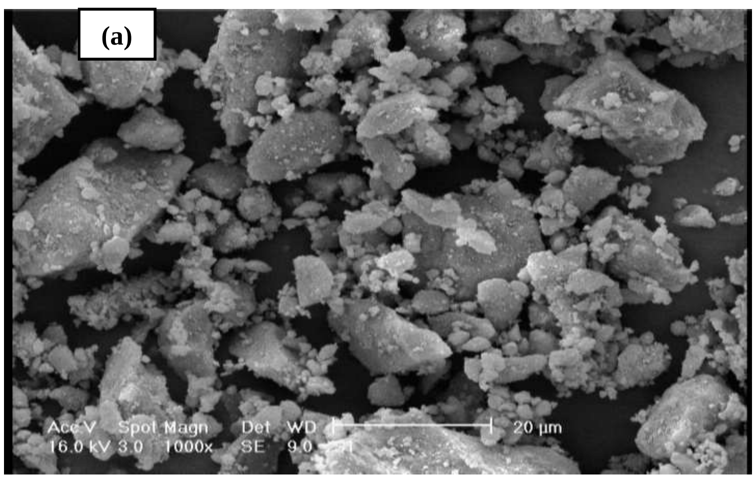
| Elements | Units | Spent catalyst | Elements | Units | Spent catalyst |
|---|---|---|---|---|---|
| Ag | ppm | 10 | Nb | ppm | 399 |
| Al | % | 39.4 | Ni | ppm | 598 |
| As | ppm | 41 | P | % | <0.1 |
| Ba | ppm | 17 | Pb | ppm | <20 |
| Be | ppm | 0.8 | Rb | ppm | 3.8 |
| Bi | ppm | <5 | S | % | 0.50 |
| 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 |

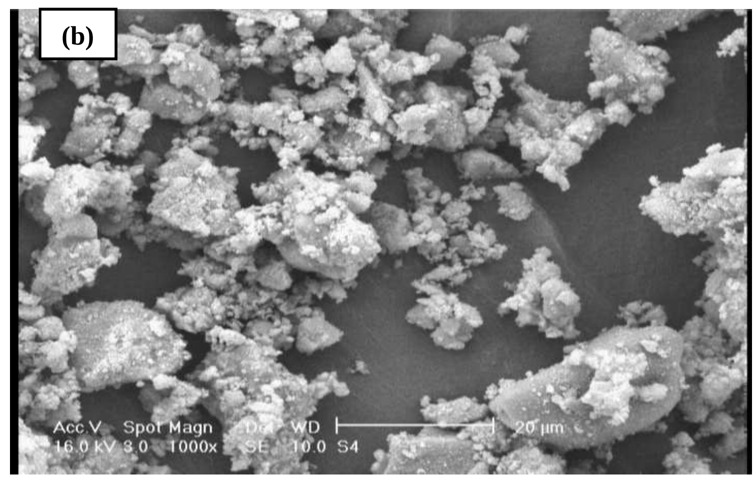
# Results & discussion

- Determination of the catalyst surface morphology by SEM (Scanning Electron Microscope)

✓ **Fig. (a) spent catalyst** extrudal shape of the catalyst with considerable variation in particle size

✓ **Fig. (b) bioleached spent catalyst** small broken particles, due to the effect of bioleaching



# Bioleaching studies

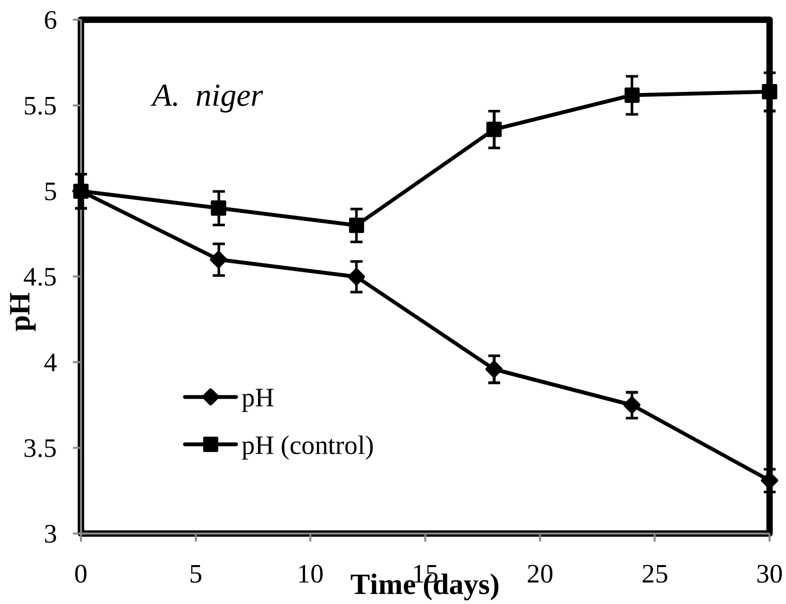
- Removal of heavy metals in the one-step process using *A. niger* and *P. simplicissimum :*

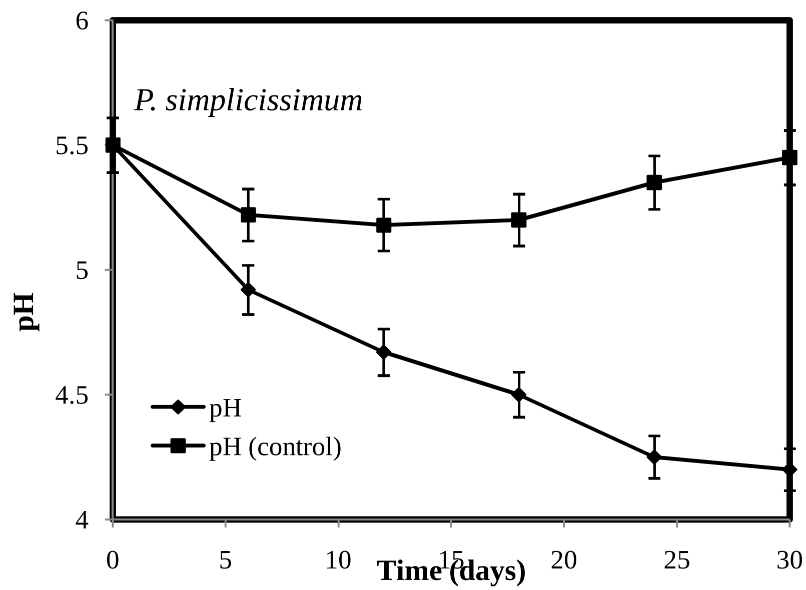
✓ *Growing A. niger & P. Simplicissimum in the presence of the spent cat. at the optimized values obtained by RSM*

| Fungi | Pulp density (g/L) | Inoculation percent (%) | pH | T (°C) | Speed of rotation (rpm) |
|---|---|---|---|---|---|
| *niger .A* | 1.8 | 9 | 5.5 | 32 | 118 |
| *P. simplicissimum* | 2 | 7 | 5.5 | 32.5 | 130 |

## Variation of pH values in the one-step bioleaching process under optimum conditions using *A. niger* & P. *simplicissmum*.

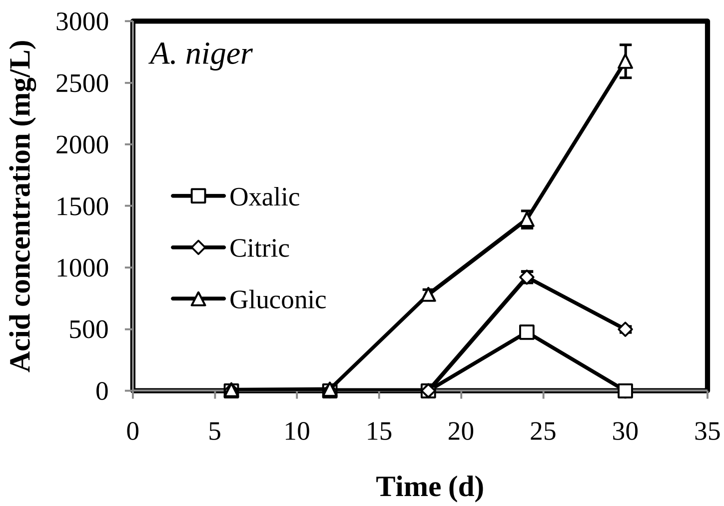
- Addition of the contaminated spent cat. resulted in some toxicity to fungal growth
- pH decrease caused by the excreted metabolites ($H^+$ & organic acids) produced by the fungi
- Reduction of pH in bioleaching process was greater than control

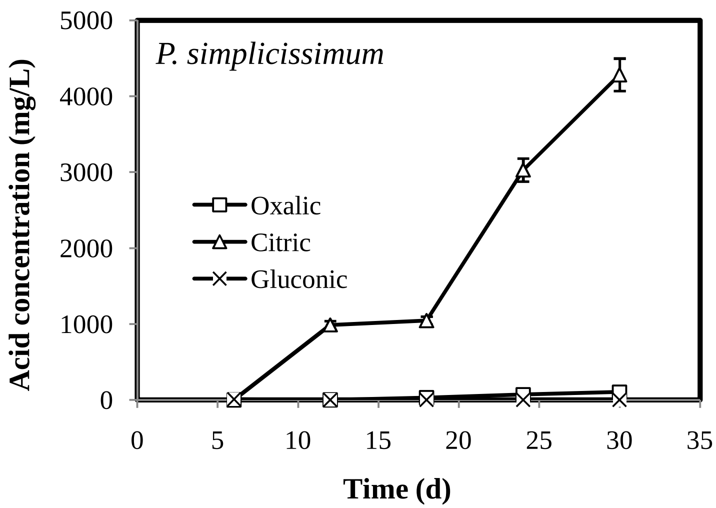


# Organic acids production

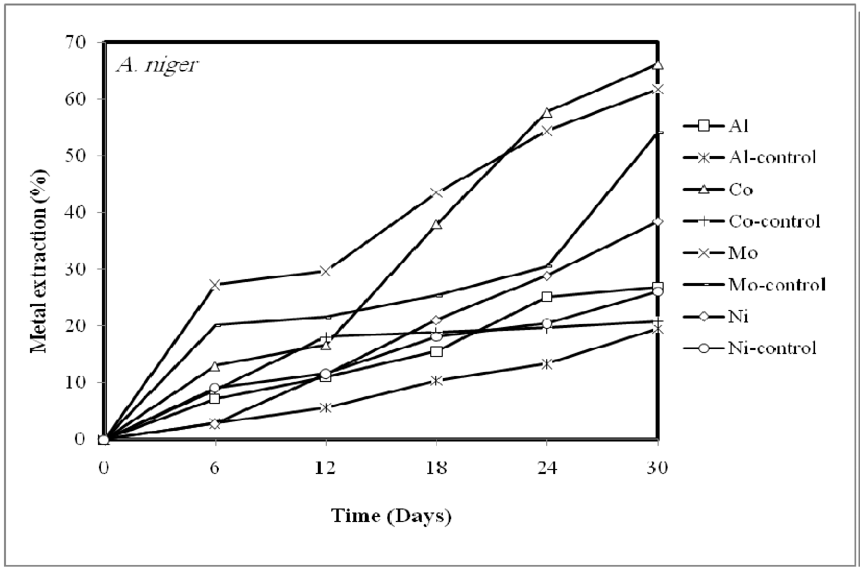
| Fungi | Gluconic (mg/L) | Citric (mg/L) | Oxalic (mg/L) |
|---|---|---|---|
| *A. niger* | 2676.4 | 922.5 | 474.9 |
| *P. simplicissimum* | negligible | 4282.6 | 108.4 |

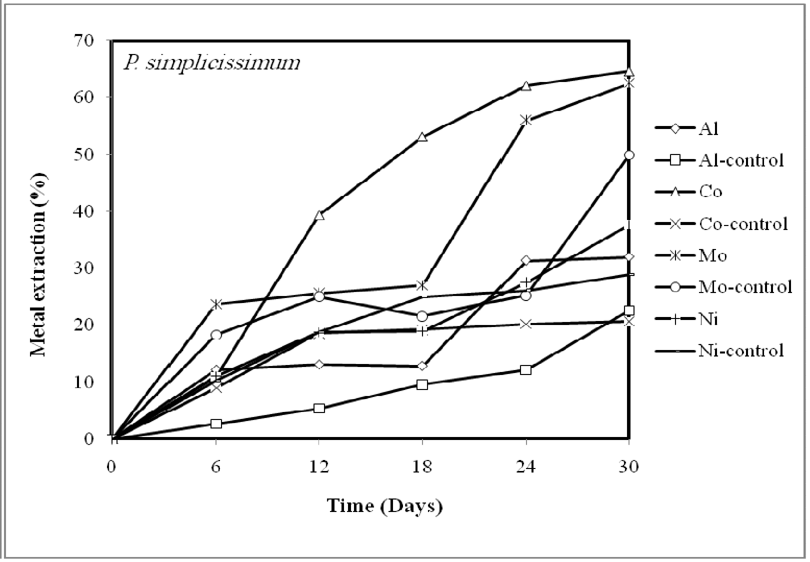


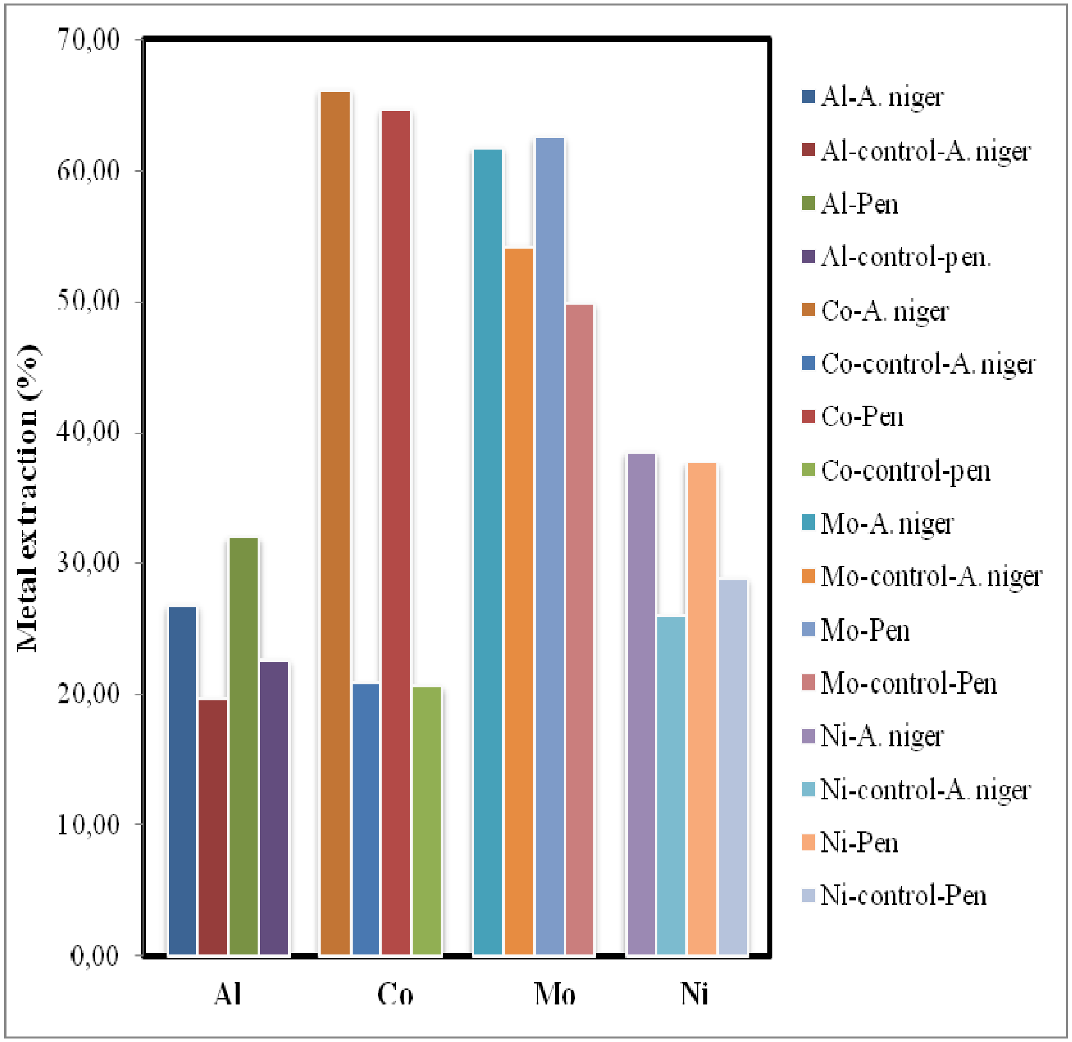
# Metal leaching efficiency by fungi

- increase in the leaching of heavy metals paralleled the increase in the concentration of organic acids
- produced organic acids played a direct and important role in the bioleaching process
- decrease in leaching efficiency beyond the maximum is probably due to the precipitation of unknown insoluble products
- 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



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



# Conclusions

- one-step bioleaching processes using either *A. niger* or *P.* ... of ...

| Fungi | Al recovery (%) | Co recovery (%) | Mo recovery (%) | Ni recovery (%) |
|---|---|---|---|---|
| niger .A | 27 | 66 | 62 | 38 |
| P. simplicissimum | 32 | 67 | 65 | 38 |

- ... les ... the ... the metals deposited on the surface of the catalysts
- for *A. niger* an increase in the conc. of gluconate increased bioleaching of metals
- in the case of *P. simplicissimum* , citrate was predominant in bioleaching process
- 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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# Thank you for your attention