

*Proceedings of the XI International Seminar on
Mineral Processing Technology (MPT-2010)*
Editors: R. Singh, A. Das, P.K. Banerjee, K.K. Bhattacharyya and N.G. Goswami
© NML Jamshedpur, pp. 946–954

LEACHING OF NICKEL LATERITE USING FUNGUS MEDIATED ORGANIC ACID AND SYNTHETIC ORGANIC ACID: A COMPARATIVE STUDY

S.K. Behera, L.B. Sukla and B.K. Mishra

Bioinorganics Department, Institute of Minerals and Materials Technology,
Bhubaneswar - 751013, India

ABSTRACT

A huge amount of overburden (nearly 8 to 10 times of the ore) containing trace amount of nickel and cobalt is generated during Chromite mining at Sukinda valley, Orissa, Chromite overburden contains around 0.4 to 0.9% Ni and 0.02–0.05% Co respectively. The setting up of nickel and cobalt processing plant based on these deposits through conventional methods such as pyrometallurgy and hydrometallurgy is not economical. The microbes and metals interaction have been studied for the exploitation in metals extraction. So an attempt has been made to extract these metals using multi metal resistant indigenous microorganisms, isolated from the Chromite overburden of Sukinda mines. A native strain of *Aspergillus species* was used for bioleaching. *Aspergillus species* are well known for their potential to produce a variety of organic acids (oxalic, citric acids etc.).

The mineralogical studies indicated that there is no separate nickel bearing mineral phase in the Sukinda Chromite overburden. The mineralogy of the raw lateritic ore reveals the presence of goethite, ferrihydrites as major minerals. In the thermally activated overburden the minerals present were hematite, surimarite, quartz and traces of magnetite. Experiments were carried out with synthetic organic acids at 2.5% pulp density, 35°C and 150rpm. Synthetic oxalic acid (0.1 M) leached 5% Ni and 71% Co from raw ore, whereas it leached 43% Ni and 95% Co from thermally activated ore. Citric acid (0.1 M) was not that much efficient. It leached 9% Ni and 14% Co from raw ore and 32% Ni and 45% Co from thermally activated ore. The fungal culture filtrate leached 3% Ni and 12% Co from raw ore. In case of roasted ore it leached 18% Ni and 28% Co at 2.5% pulp density, 35°C and 150rpm. Mineralogical analysis was carried out through X-ray diffraction, FTIR and transmission electron microscopy.

Keywords: Chromite overburden, Nickel, Cobalt, *Aspergillus sp.* Organic acid.

INTRODUCTION

Nickel and cobalt are industrially important metals widely used in aviation, automobile and steel industries. The growing economy of India demands huge nickel and cobalt resources for its industrial and infrastructural expansion. As Indian demand for these noble metals basically depends upon import, so the waste generated as chromite overburden at Sukinda valley, Orissa during chromite mining would be a potential source of nickel and cobalt. One attractive way to utilize the low grade nickel lateritic ore is to dissolve the nickel and cobalt by the metal chelating

and solubilising organic acids secreted by the heterotrophic microbes (Tang and Valix, 2006). The fungi e.g. *Aspergillus*, *Penicillium species* have been reported for the secretion of organic acids (like oxalic acid and citric acid etc.) as metabolic by products during the growth (Gadd, 1999). These organic acids have the potential of metal solubilisation and chelation. (Alibhai *et al.*, 1992; Bosecker, 1985; valix *et al.*, 2001).

Fungi are well known to tolerate and detoxify metals by several mechanisms including valence transformation, extra- and intracellular precipitation, and active uptake (Birch and Bachofen, 1990; Joho *et al.*, 1995; Tebo, 1995; Volesky, 1988). Recently, several fungi have been reported to precipitate metals such as cobalt, copper, zinc, manganese, and strontium as oxalate, citrate, or pyruvate crystals (Gadd, 1999; Gharieb *et al.*, 1998; Sayer and Gadd, 1997; Sayer *et al.*, 1997). The passive metal removal or biosorption is also common among microorganisms (Al-Asheh and Duvnjak, 1995; Kapoor and Viraraghaven, 1998a; Mogollon *et al.*, 1998; Tobin *et al.*, 1984; Volesky, 1988; Yetis *et al.*, 1998).

In India, particularly in Sukinda mines Orissa, a huge amount of overburden is generated during chromite ore mining, which contains 0.5–1% nickel and 0.03–0.04% cobalt (Mohapatra *et al.*, 2007). In this present study, with a view to develop a economic process to recover these valuable metals from this chromite overburden, studies were carried out using synthetic organic acids (oxalic and citric acid) as leaching agent for nickel and cobalt recovery and compared with the leaching potential of fungal strain *A. fumigatus* for nickel and cobalt recovery. Further the thermally pre treatment (600°C) of the chromite over burden have significant influence on nickel and cobalt recovery (Valix and Cheung, 2002). The pre treatment changes the mineral structure and brings the mineral phase transformation by dehydroxylation of the goethite matrix (Jinhui *et al.*, 2009).

EXPERIMENTAL

Materials

Chromite Overburden Samples

Chromite overburden samples were obtained from major chromite deposits of Sukinda Mines, Orissa, India. In this overburden, nickel is reported to be associated with the goethite iron matrix and cobalt is associated with the manganese phase (Sukla and Das, 1987). The leaching experiments were carried out by two different forms of the overburden samples, they were designated as original chromite over burden, the second form is pre treated chromite overburden (roasted) at 600°C for 5 hours to convert the nickel bearing iron phase goethite to hematite in order to release the nickel from the goethite matrix (Mohapatra *et al.* 2008).

Table 1: Metal Composition (%) In original chromite overburden and roasted chromite overburden of Sukinda mines, Orissa

	Metal Composition (%) in different types of chromite overburdens				
	Nickel	Cobalt	Iron	Chromium	Manganese
Original chromite over burden	0.99	0.03	48.88	2.59	0.21
Roasted chromite over burden	1.02	0.04	50.85	3.65	0.35

Fungal strain & culture medium

The fungal strain i.e. *Aspergillus fumigatus* used in this experimental study was a laboratory stock culture isolated from chromite overburden. The fungal cultures were preserved at 4°C on potato dextrose agar slants. Bromofield medium that was used for the fungal leaching contains of (g/L): MgSO₄ 7H₂O-0.75, KH₂PO₄- 0.25, (NH₄)₂SO₄- 0.25, yeast extract- 1, sucrose-20. The pH of the media was adjusted to 6.8. The spore suspension of 5 to 7 days old culture was used as inoculums.

Fungal mediated bio-acids (FMBAs)

The fungal bio-acids were prepared by culturing fungus *A. fumigatus* in bromofield medium. The carbon source, sucrose present in the culture medium is quantitatively converted to FMBAs, through different biochemical pathways which eventually lowers the pH of the medium. The FMBAs was harvested after maximum utilization of the sucrose in the culture medium by *A. fumigatus*. The sucrose concentration was quantified by Anthron reagent method. Further the FMBAs were identified and quantified by HPLC.

Synthetic organic acids

Organic acids (oxalic & citric acids) were taken from analytical grade for the leaching experiments.

Methods

Shake flask leaching

Leaching experiments were carried out in 250 ml of the Erlenmeyer flask and kept in rotary shaker (150 rpm). The chromite overburdens used in these experiments were crushed to an average size 63–75 micron. Leaching experiments were carried out by *A. fumigatus*, FMBAs produced by fungus *A. fumigatus* and synthetic organic acids (oxalic & citric acid) by keeping organic acid concentration at 0.1 M with keeping pulp density at 2.5%. The leaching experiments were performed for an incubation period of 20 days at 35°C. After completion of the experiment the leach liquor was separated through 0.45 micron membrane filter and the filtrate was analyzed for nickel and cobalt by Perkin Elmer (Model AA -200) atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

Fungal mediated bio-acids analysis

The culture filtrate was harvested for organic acids analysis carried out after maximum consumption of sucrose by *A. fumigatus*. Then the organic acid content of culture filtrate was analyzed by HPLC. The Agilent 1100 (Agilent technologies, Waldbronn Analytical Division, Germany) which consists of column (Zorbax Eclipse XDB-C18, 150 × 4.6 mm, i.d) were used for analysis. Standards have been taken from HPLC grade. Prominent carboxylic acids such as oxalic acid and citric acid are detected in culture filtrate after maximum utilization of the sucrose by *A. fumigatus* strain. Analysis for organic acid content carried out with triplicate samples, an about 0.76%–0.81% citric acid and 0.72–0.77% oxalic acid was detected in the culture filtrate of *A. fumigatus* strain.

Electron Probe Micro Analyzer (EPMA) Study of Chromite overburdens

The compositional and distributional map of different elements in chromite overburdens are analyzed under EPMA (JEOL, JXA-8100). In the original chromite overburden sample Ni and Co are observed to be confined within Fe and Cr-phases. In case of the pre treated overburden sample (at 600°C) most of the goethite gets converted to hematite.

The X-ray diffraction study of Chromite overburdens

The X-ray diffraction study (Fig. 1) was carried out by means of Phillips Diffractometer (PW3710) with a radiation operating at 40 kV and 30 mA. The raw overburden reveals the presence of the goethite, a hydrated iron oxide (α -FeOOH) where as in case of the roasted sample the goethite form is converted to the hematite Fe_2O_3 form due to calcinations.

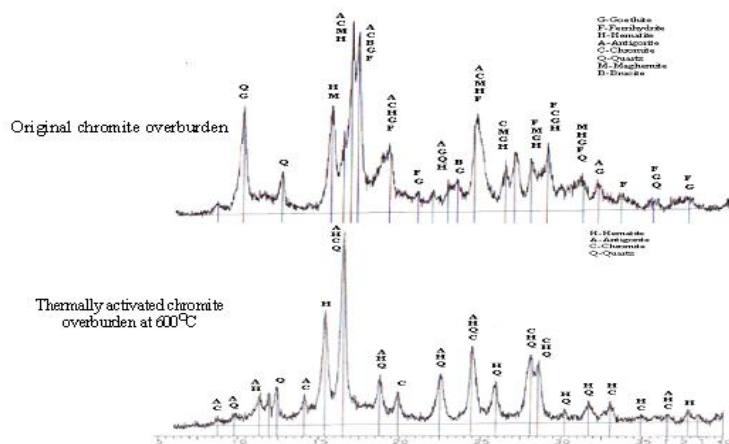


Fig. 1: X-ray diffraction analysis of chromite overburdens.

FTIR spectroscopy study

Fourier-transform infrared (FTIR) spectral studies were carried out with a *Perkin Elmer (Model Spectrum 1)* spectrophotometer in the range between $4000\text{--}400\text{ cm}^{-1}$, with a resolution of 2 cm^{-1} . The structure of the goethite (iron oxide) in original chromite overburden (Fig. 2a) and hematite was identified by FTIR spectroscopy. FTIR results showed that the different compounds exhibited peak characteristics of both goethite and hematite. The hematite particles which formed by dehydration and reordering of the internal bonds of the goethite iron oxide samples during the thermal activation were spheroidal. Hematite formed during treatment of the lateritic nickel ore gave broad IR band centered at 533 and 454 cm^{-1} (Fig. 2b) (Vempati *et al.*, 1990), and similar type of vibration can be seen in FTIR spectroscopy of the natural hematite (Fig. 2c). The decrease in band intensity and shift in band centre from 3155 cm^{-1} to 3400 cm^{-1} is indicative of the transformation of structure from goethite to hematite. While the remaining 2924 cm^{-1} band in the newly formed hematite (Fig. 2c and 2b) is the vibration of non-stoichiometric hydroxyl units that transferred directly from goethite to hematite (Ruan *et al.*, 2002). This structural alteration

indicated by hydroxyl units is obviously observed only in the FTIR spectra compared with the XRD technique. The band at 3409 cm^{-1} (Fig. 2b) in the hydroxyl stretching region remained (3155 cm^{-1}) after the completion of goethite-hematite transformation. This indicates that goethite altered to hematite without intermediate phases and the newly formed hematite inherited the remaining non-stoichiometric hydroxyl units from the precursor goethite.

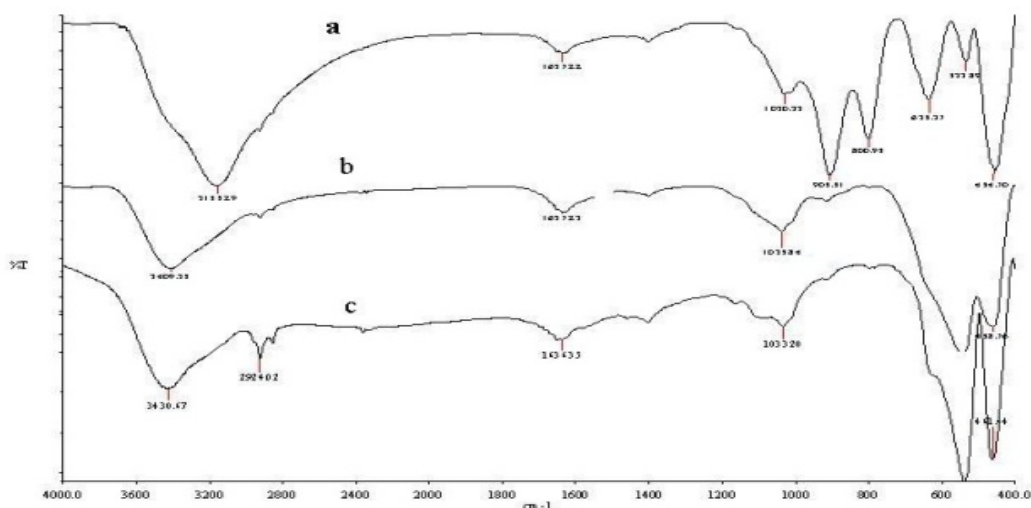


Fig. 2: FTIR spectroscopic analysis of chromite overburdens.

Shake flask leaching

Fungus A. fumigatus mediated bioleaching

The leaching experiments were carried out in 250 ml Erlenmeyer flasks containing 100 ml of bromofield media and chromite overburden samples at 2.5% pulp density. Each flask was inoculated with 10 ml of spore suspension of the respective ore-adapted fungal strain. All flasks were incubated at 30°C on a rotary shaker. The flasks were harvested after 20 days. The contents of the flasks were filtered and the fungal biomass and ore residue were washed with 1% hydrochloric acid. The resulting solutions were appropriately diluted and were analyzed by AAS to determine the percentage of nickel and cobalt recovered by the fungal strain *A. fumigatus*.

A. fumigatus leached 38% of nickel and 95 % cobalt in 20 days (Figs. 3 and 4) from pre treated chromite overburden at 2.5% pulp density. Whereas with original chromite overburden the nickel recovery is 10% and cobalt recovery achieved was 18 %, at 2.5 % pulp density.

Fungus Mediated Bio Acids (FMBAs) leaching

To evaluate the leaching potency of FMBAs by *A. fumigatus* for nickel and cobalt recovery from chromite overburdens, the leaching study was carried out. Then nickel and cobalt leaching from the chromite overburdens performed in FMBAs at shake flask scale with 2.5% pulp density of chromite overburden. All flasks were incubated at 30°C on a rotary shaker; the flasks were harvested after 20 days. Liquid samples were taken at the end, filtered through 0.45 micron

membrane filter, and analyzed for nickel and cobalt dissolved in each sample by atomic absorption spectrophotometer. About 14% nickel and 41% cobalt (Figs. 3 and 4) recovered at 2.5% pulp density of pre treated chromite overburden using FMBA's leaching, in case of original chromite overburden 5% nickel & 10% cobalt recovered.

Synthetic Organic acid leaching

Synthetic organic acid like oxalic and citric acids are taken to evaluate their leaching potency of chromite overburdens. Different chromite overburdens are leached at 2.5 % pulp density kept in rotary shaker mentioned at 150 rpm at 30°C. Figs. 3 and 4 shows that 38% nickel and 97% cobalt recovery from pre treated chromite overburden in oxalic acid (0.1M) leaching. Where as 5% nickel and 59% cobalt was recovered from original chromite overburden. In citric acid (0.1 M) leaching (Figs. 3 and 4), nickel and cobalt recovery from pre treated chromite overburden was 21% and 30% respectively.

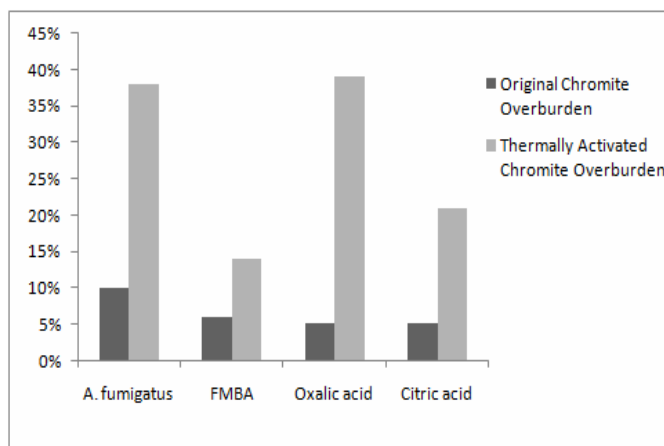


Fig. 3: Nickel recovery from different Chromite overburdens

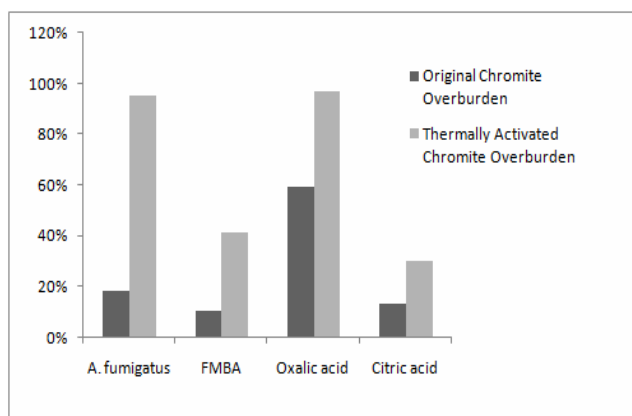


Fig. 4: Cobalt recovery from different Chromite overburdens

Microorganisms are capable of dissolving heavy metals from the ores by their intermediate or end products metabolism such as organic acids and metabolites. Microbially produced organic acids are thought to operate by two mechanisms:

1. Hydrogen ions can displace metal cations from the ore matrix and thus induce dissolution of metals.
2. Organic acids can sequester metals into soluble metal ligand complexes by chelation.

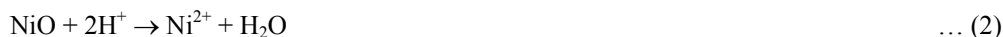
The ability of microorganisms to leach and mobilize metals from solids materials comprises 3 principles namely:

- (a) Redox reactions
- (b) Formation of organic or inorganic acids,
- (c) Excretion of complexing agents (Krebs *et.al.*, 1997).

Acid Production



Acid Leaching



Complexation/Chelation of Ni with Citric acid



Precipitation by Oxalic acid



Enhanced recovery of nickel and cobalt obtained in case of the pre treated chromite overburden in compare to original chromite overburden during leaching processes. As majority of nickel present in the lattice of the iron oxide matrix of chromite overburden, the recovery of the nickel during leaching directly proportional to the dissolution of iron matrix by carboxylic acids. The oxalic acids show more potential to solubilise the iron oxide matrix than the citric acid so higher nickel recovery achieved in case of oxalic acid leaching. Enhanced recovery of nickel and cobalt obtained during leaching processes in case of pre treated chromite overburden due to higher solubility of iron phase present. The higher metal recovery in case of direct heterotrophic leaching by *A. fumigatus* obtained due to metal solubilization by secretory carboxylic acids as well as metal uptake by the fungal cell itself (Magyarosy *et al.*, 2002). Where as in case fungal bio-acid leaching of the chromite over burdens the metal leaching agents are the only carboxylic acids present in fungal bio-acids.

CONCLUSION

EPMA analysis reveals the homogeneous distribution of nickel and cobalt on pre treated chromite overburdens. The XRD and FTIR analysis shows that thermal activation of chromite overburdens at 600°C alters the goethite matrix to a thermodynamically stable configuration of hematite phase

due to dehydroxylation and thermo-chemical mechanism. Oxalic acid, one of the prominent organic acids in FMBAs has more potential to leach nickel and cobalt from chromite overburdens. At 2.5% pulp density of pre treated chromite overburden, maximum nickel and cobalt recovery were about 38% & 95% respectively by *A. fumigatus* 38% (Ni) & 97% (Co) in oxalic acid (0.1M), 21% (Ni) & 30% (Co) in citric acid (0.1M) and 14%(Ni) & 41% (Co) in FMBAs leaching, in compare to original chromite overburdens.

ACKNOWLEDGEMENT

The authors are genuinely gratified to Council of Scientific and Industrial Research for its constant financial support. One of the authors would like to acknowledge CSIR for Junior Research Fellowship. We thankful to Dr. S.K. Sahoo, Institute of Life Sciences, Bhubaneswar, for performing FTIR analysis in this study.

REFERENCES

- [1] Al-Asheh, S. and Duvnjak, Z., 1995, Adsorption of copper and chromium by *Aspergillus carbonarius*. *Biotech Prog* 11, p. 638.
- [2] Alibhai, K., Leak, D., Dudeney, A.W.L. and Agatzini, S., 1992, Microbial leaching of nickel from low-grade Greek laterites. *Proceedings of Mineral Processing*, Engineering Foundation of USA, Santa Barbara, July, p. 191.
- [3] Gadd, G.M., 1999, Fungal production of citric and oxalic acid: importance in metal speciation, physiology and biogeochemical processes. *Adv Micro Phys* 41, p. 47.
- [4] Henderson, M.E.K. and Duff, R.B., 1963, The release of metallic and silicates ions from minerals, rocks, soils by fungal activity. *J. Soil Sci.* 14, p. 236.
- [5] Jinhui, L., Xinhai, L., Qiyang, H., Zhixing, W., Youyuan Z., Junchao, Z., Wanrong, L. and Lingjun, L., 2009, Effect of pre-roasting on leaching of laterite. *Hydrometallurgy* 99, p. 84
- [6] Joho, M., Inohue, M., Tohoyama, H. and Murayama, T., 1995, Nickel resistance mechanisms in yeasts and other fungi. *J Indust Microbiol* 14, p. 164.
- [7] Magyarosy, A., Laidlaw, R.D., Kilaas, R., Echer, C., Clark, D.S. and Keasling, J.D., 2002, Nickel accumulation and nickel oxalate precipitation by *Aspergillus niger*. *Appl Microbiol Biotechnol.* 59, 382–388.
- [8] Mohapatra, S., Sengupta, C., Nayak, B.D., Sukla, L.B. and Mishra, B.K., 2009, Biological leaching of nickel and cobalt from lateritic nickel ore of Sukinda mines. *Korean J. Chem. Eng.*, 26 (1), p. 108 .
- [9] Mohapatra, S., Sengupta, C., Nayak, B.D., Sukla, L.B. and Mishra, B.K., 2008, Effect of thermal pretreatment on nickel and cobalt from Sukinda lateritic nickel ore using microorganisms. *Korean J. Chem. Eng.*, 25 (5), p. 1070.
- [10] Ruan, H.D., Frost, R.L., Kloprogge, J.T. and Duong L., 2002, Infrared spectroscopy of goethite dehydroxylation. II. Effect of aluminium substitution on the behaviour of hydroxyl units. *Spectrochimica Acta Part A.* 58, p. 479.
- [11] Ruan, H.D., Frost, R.L., Kloprogge, J.T. and Duong L., 2002, Infrared spectroscopy of goethite dehydroxylation: III. FT-IR microscopy of in situ study of the thermal transformation of goethite to hematite. *Spectrochimica Acta Part A.* 58, p. 967.

- [12] Sayer, J.A. and Gadd. G.M., 1997, Solubilization and transformation of insoluble inorganic metal compounds to insoluble metal oxalates by *Aspergillus niger*. *Mycol Res* 101, p. 653.
- [13] Sayer, J.A., Kierans, M. and Gadd, G.M., 1997, Solubilisation of some naturally occurring metal-bearing minerals, limescale and lead phosphate by *Aspergillus niger*. *FEMS Microbiol Lett* 154, p. 29.
- [14] Valix, M., Usai, F. and Malik, R., 2001, Fungal Bioleaching of low grade nickel laterite ores. *Minerals Engineering.*, 14 (2), p. 197.
- [15] Valix, M. and Cheung, W.H., 2002, Study of phase transformation of laterite ores at high temperature. *Miner. Eng.* 15, p. 607.
- [16] Vempati, R.K., Loeppert, R.H., Sittertz-Bhatkar, H. and Burghardt, R.C., 1990, Infrared vibrations of hematite formed from aqueous-and dry- thermal incubation of Si-containing ferrihydrites. *Clays and Clay Minerals*, **38**, No. 3, 294.
- [17] Volesky, B., 1988, Removal and recovery of metals by biosorbent materials. *Biotechnology* 2, p. 135.