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Recovery of Heavy Metals from Indian LD slag Using Acidophilic and Heterotrophic Bacteria: A Comparative Study

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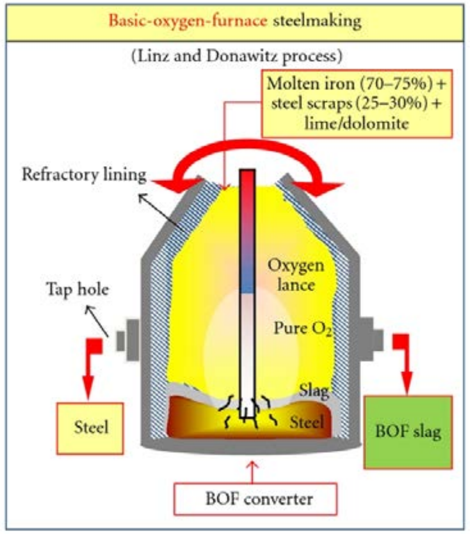
Aim of the Study

Iron and Steel Industry



- ✓ India is the 2nd largest steel producer in the world
- ✓ In 2019, crude steel production in India was 111.2 MT

Solid Waste Production

- ✓ 0.6-0.8 T solid waste generated per ton steel
- ✓ **BF slag, BOF/LD slag**, EAF slag, Dust and sludge

Almost complete utilization of BF slag as gypsum and clinker

LD/BOF Slag

- ✓ 150-200 kg LD slag generated per ton steel
- ✓ **20% of LD slag is utilized**
- ✓ **80% is discarded in landfills**

Economic loss due to landfills

Direct discharge of particles

Leaching in soil, surface & groundwater

Use in various industrial applications

Presence of metals

Chemical Leaching

Biological leaching

Removal of Metals from Slag

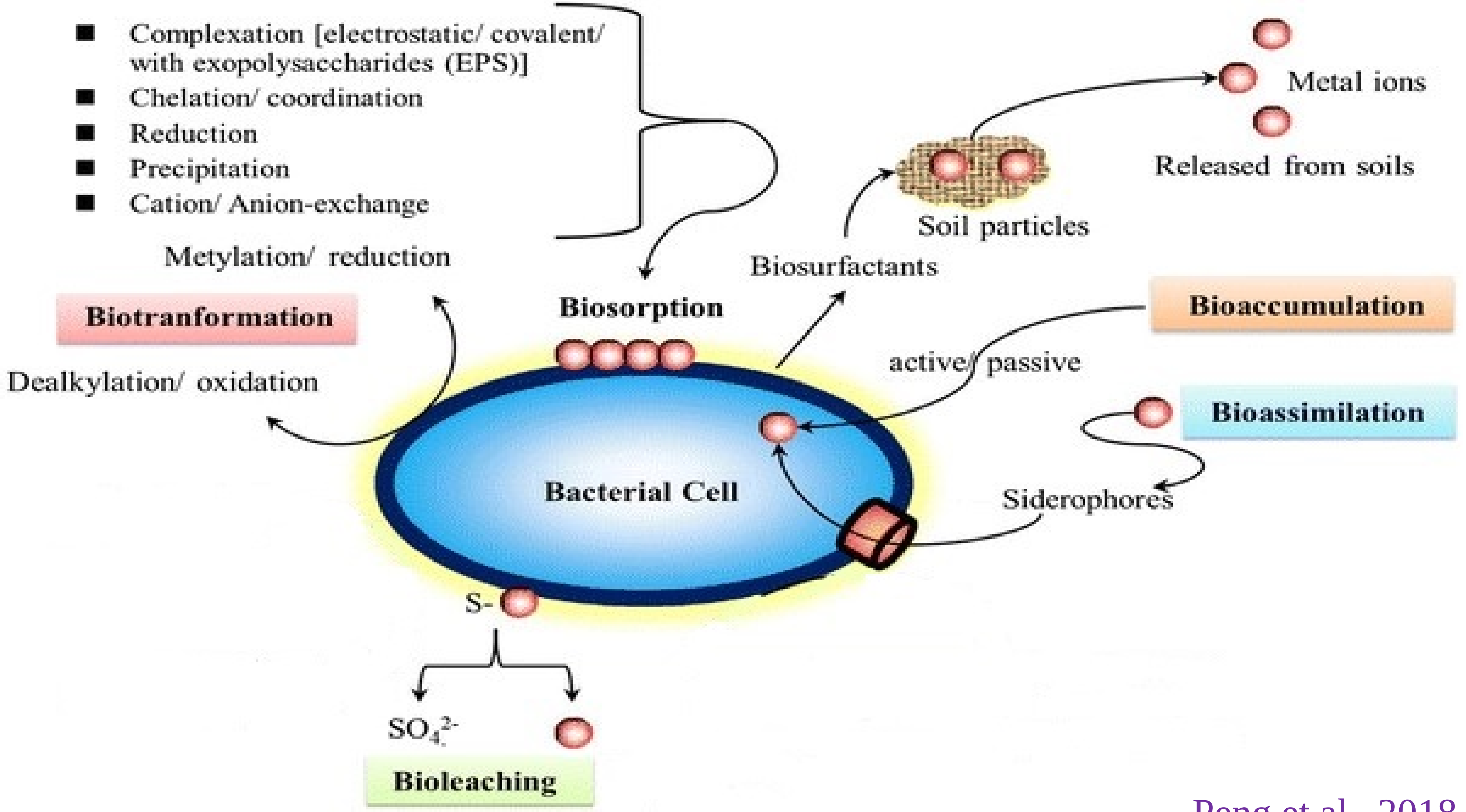
Hydrometallurgy

- Use of aqueous solutions (sulfuric and hydrochloric acid)
- Used when the metal concentration is very high
- Energy and cost intensive
- Generates hazardous waste and harmful gases

Bioleaching

- Uses microorganisms for removal of metals
- Use of autotrophic/ chemolithotrophic bacteria, heterotrophic bacteria and fungi
- Low cost and energy

Bioleaching Mechanism



Peng et al., 2018

Types of Bioleaching

Autotrophic Acidophilic Bacteria

- Uses reduced iron or sulphur (sulphides) as electron donor for the production of sulfuric acid
- No organic carbon source required
- Metal tolerant organisms that work effectively at low pH
- ***Acidithiobacillus thiooxidans, Acidithiobacillus ferrooxidans***
- $2FeSO_4 + 0.5O_2 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + H_2O$
- $4Fe_2(SO_4)_3 + 2MeS + 4H_2O + 2O_2 \rightarrow 2Me^{2+} + 2(SO_4)^{2-} + 8FeSO_4 + 4H_2SO_4$

Heterotrophic Bacteria/ Fungi

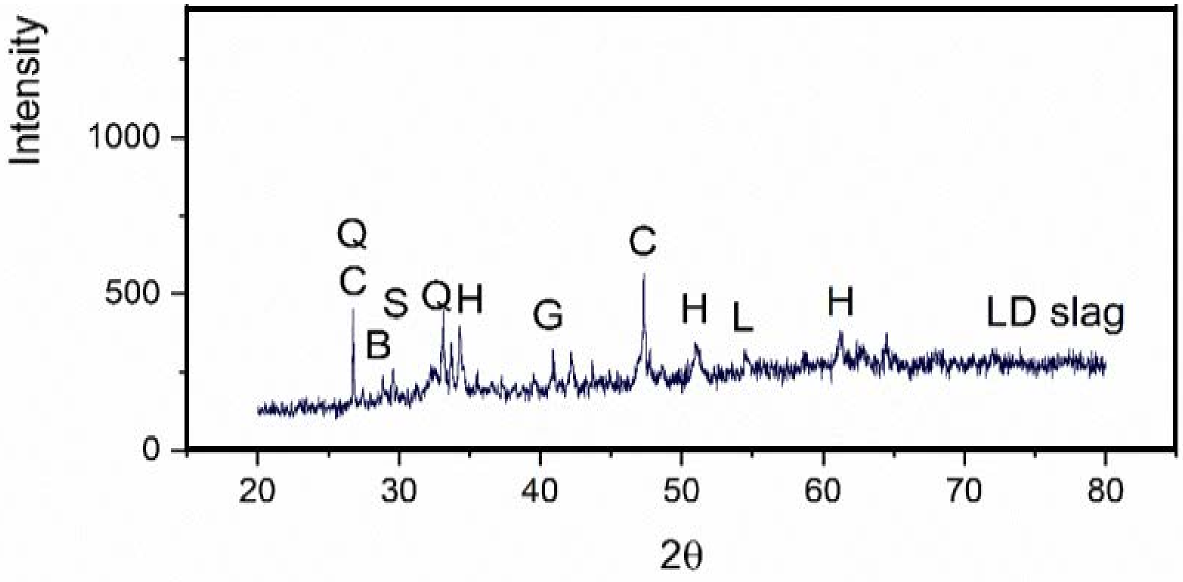
- Uses organic carbon for the production of organic acid
- Metal sensitive; works best at neutral pH
- Works on metal oxides and carbonates
- **Bacteria: *Acetobacter, Acidophilum, Arthrobactor, Pseudomonas, Trichoderma***
- **Fungi: *Penicillium, Aspergillus* and *Fusarium***

Objectives

- To characterize LD slag obtained from Tata Steel
- To determine bioleaching of toxic and valuable metals from LD slag using ***Acidithiobacillus ferrooxidans* and *Pseudomonas aeruginosa***
- To determine the mechanism of bioleaching of various metals from LD slag by acidophilic and heterotrophic microbes

Characterization of Slag

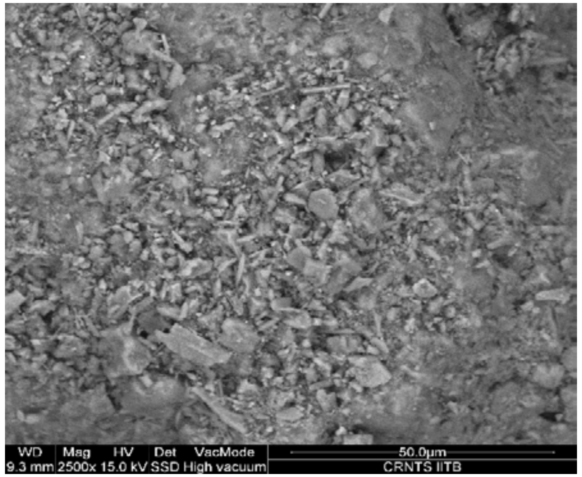
XRD Analysis



C: Calcite ($CaCO_3$)
Q: Quartz (SiO_2)
B: Burnt ochre (Fe_2O_3)
S: Silica (SiO_2)

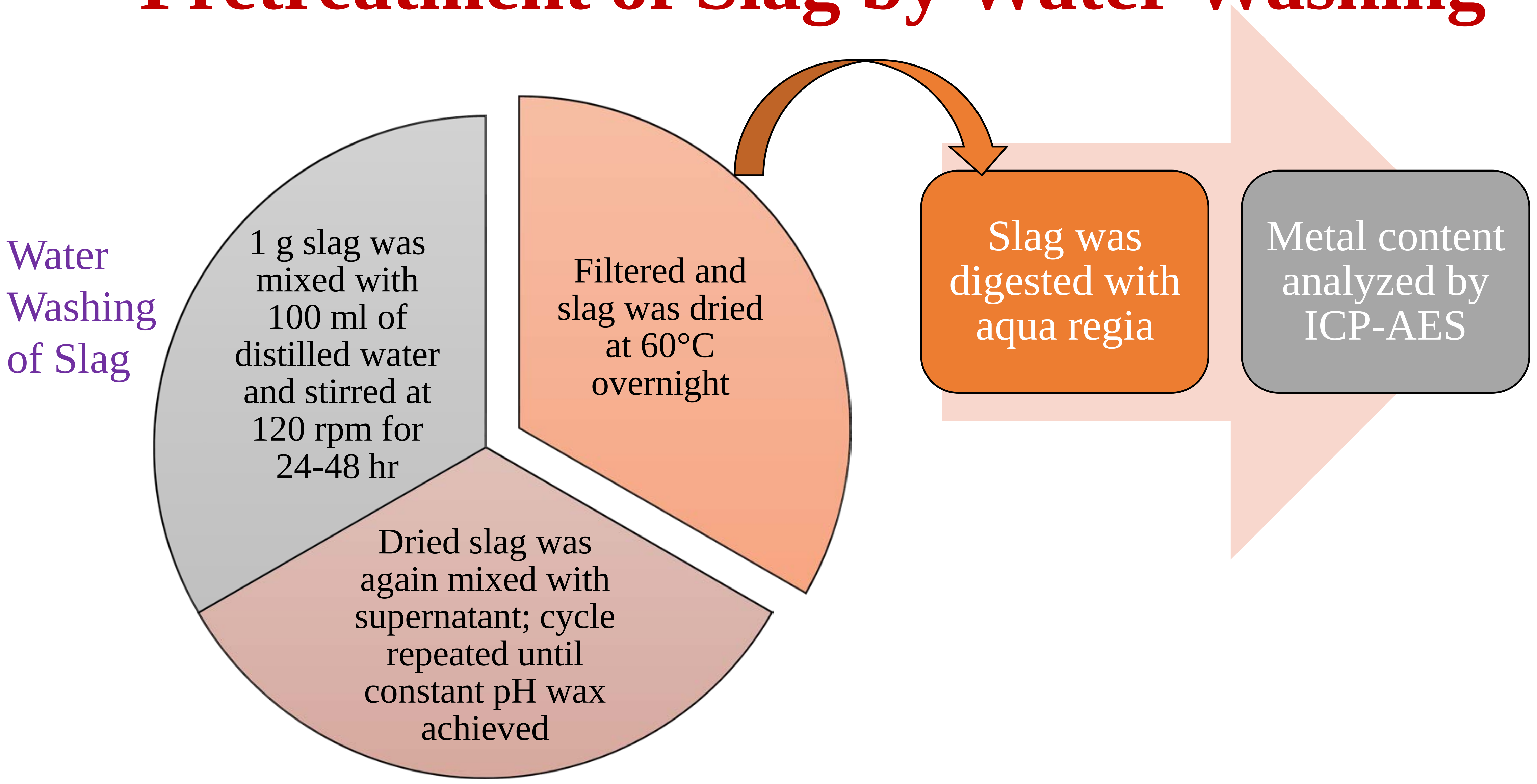
H: Hematite (Fe_2O_3)
G: Green cinnabar (Cr_2O_3)
L: Lime (CaO)
M: Magnetite (Fe_2O_3)

SEM Analysis



- pH= 13.44; Density= 1.994 g/cc
- Particle size of less than 50 µm
- EDAX: C= 26%; O=29%, Ca=31%;
- Mg=3%; Si=3%; P= 1.6%; Fe= 1.3%

Pretreatment of Slag by Water Washing



- **Water washing as pre-treatment used to lower down the pH of the slag**

Bioleaching Studies

Pre-washed slag (1 g) was mixed with mineral media (100 ml)

After adding inoculum (10%), the batch cultures were incubated for 21 days at 30°C and 120 rpm

An aliquot was withdrawn, filtered and metal analysis was done using ICP-AES

Composition	Amount (g/L)	
$(NH_4)_2SO_4$	0.5	*Acidithiobacillus ferrooxidans*
K_2HPO_4	0.5	
$MgSO_4.7H_2O$	0.5	
1 N H_2SO_4	5.0 ml	
$FeSO_4$. $7H_2O$	167.0	

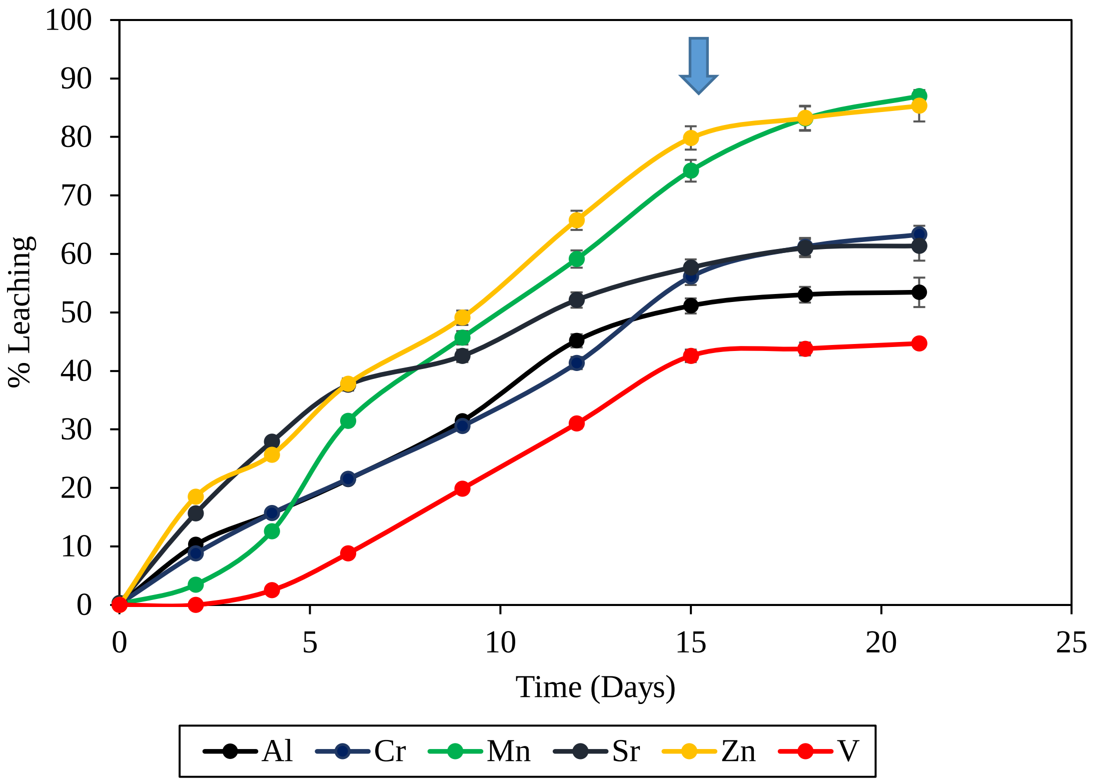
Composition	Amount (g/L)	
Peptone	20	*Pseudomonas aeruginosa*
Yeast extract	2	
Glucose	20	
KH_2PO_4	0.75	
$MgSO_4.7H_2O$	0.3	
pH	7	

Metal Quantification

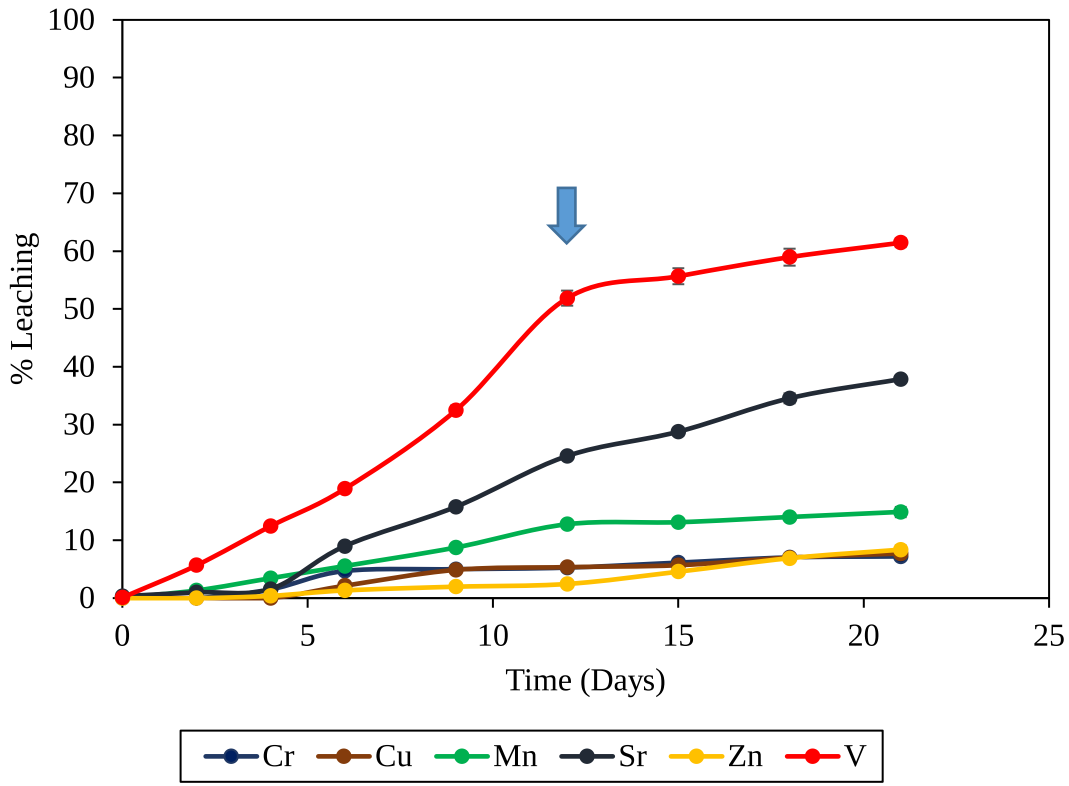
Metals	Slag conc. (mg/kg)	Soil standards (mg/kg)	Important Characteristics
TOXIC METALS			
Aluminium (Al)	**7935.00** (± 89.50)	50	Phytotoxicity
Chromium (Cr)	**710.25** (± 5.20)	<1	Carcinogenic and mutagenic effects
Copper (Cu)	**13.37** (± 0.10)	10	Micronutrient but can cause cytotoxicity
Zinc (Zn)	**29.50** (± 0.25)	5	Micronutrient, but causes phytotoxicity & metal fume fever in humans
VALUABLE METALS			
Manganese (Mn)	**3942.75** (± 28.50)	220	Alloys, Dry cell batteries
Strontium (Sr)	**148.25** (± 1.50)	0.2-64	Medicine, Ferrite magnets
Vanadium (V)	**426.12** (± 8.50)	2	Storage of renewable energy in batteries

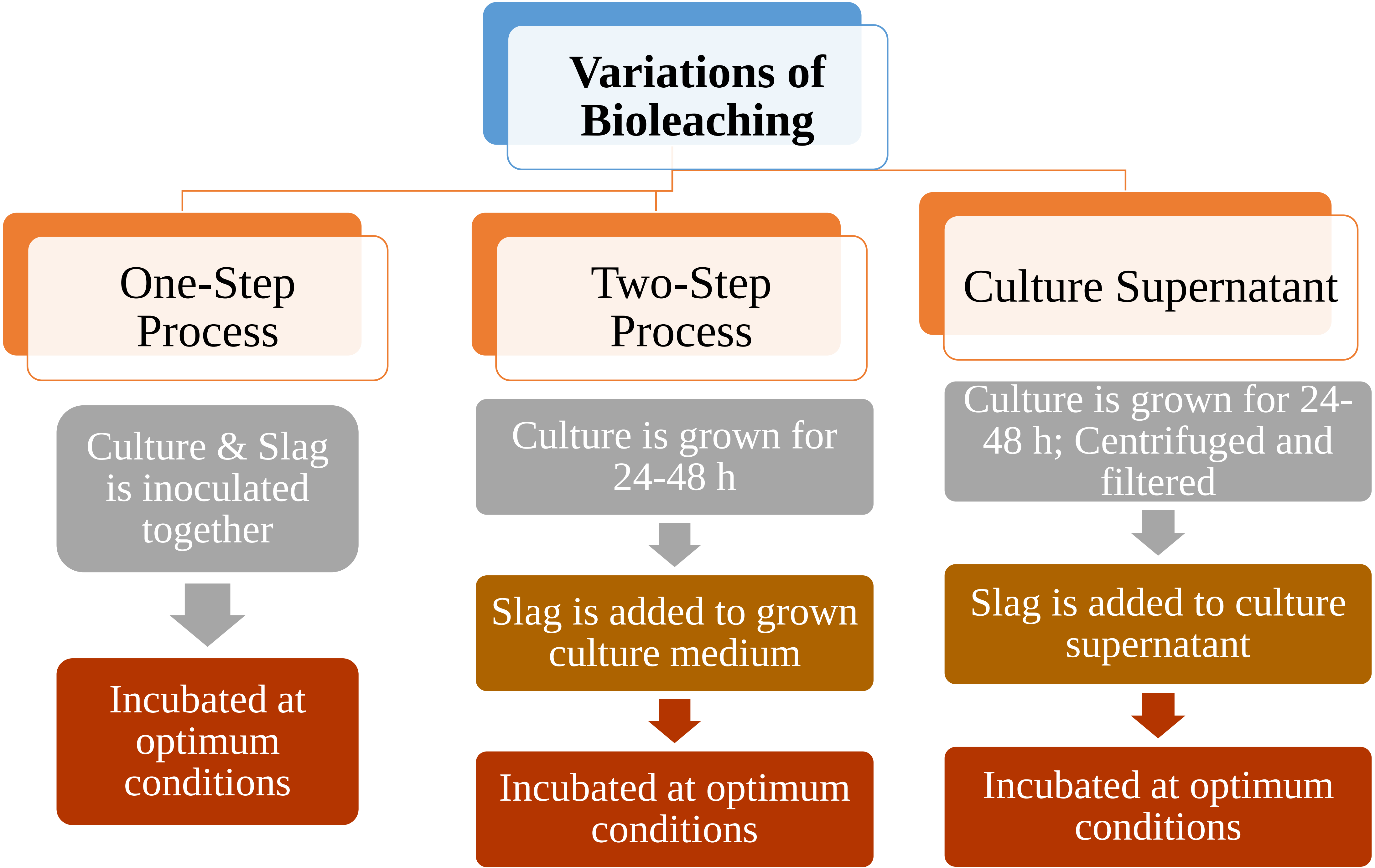
Comparison of Acidophilic and Heterotrophic Bioleaching

Acidithiobacillus ferrooxidans

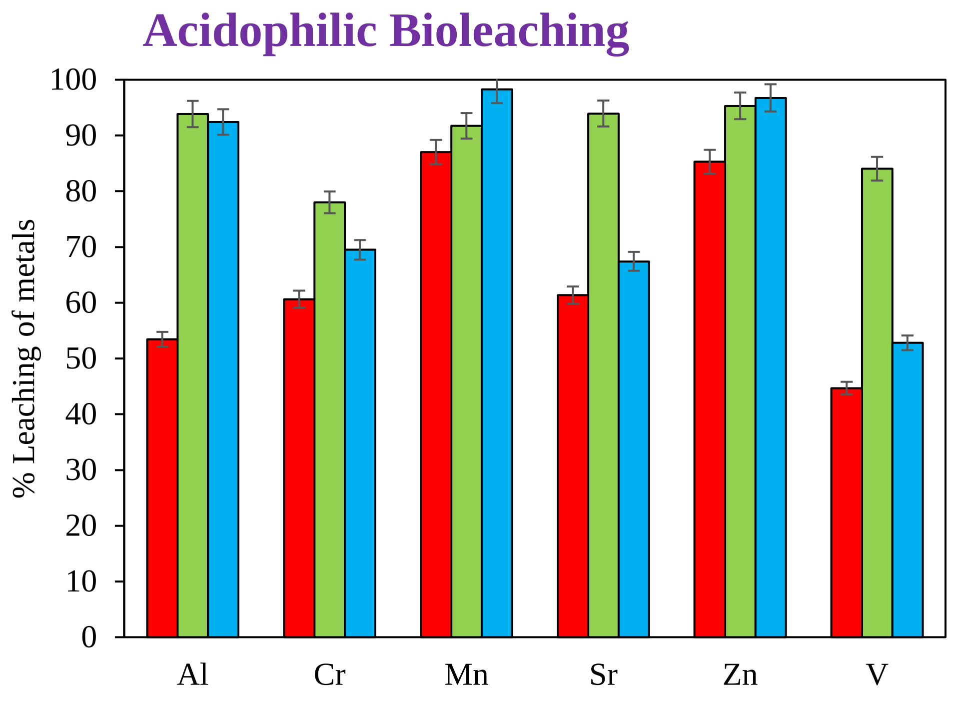


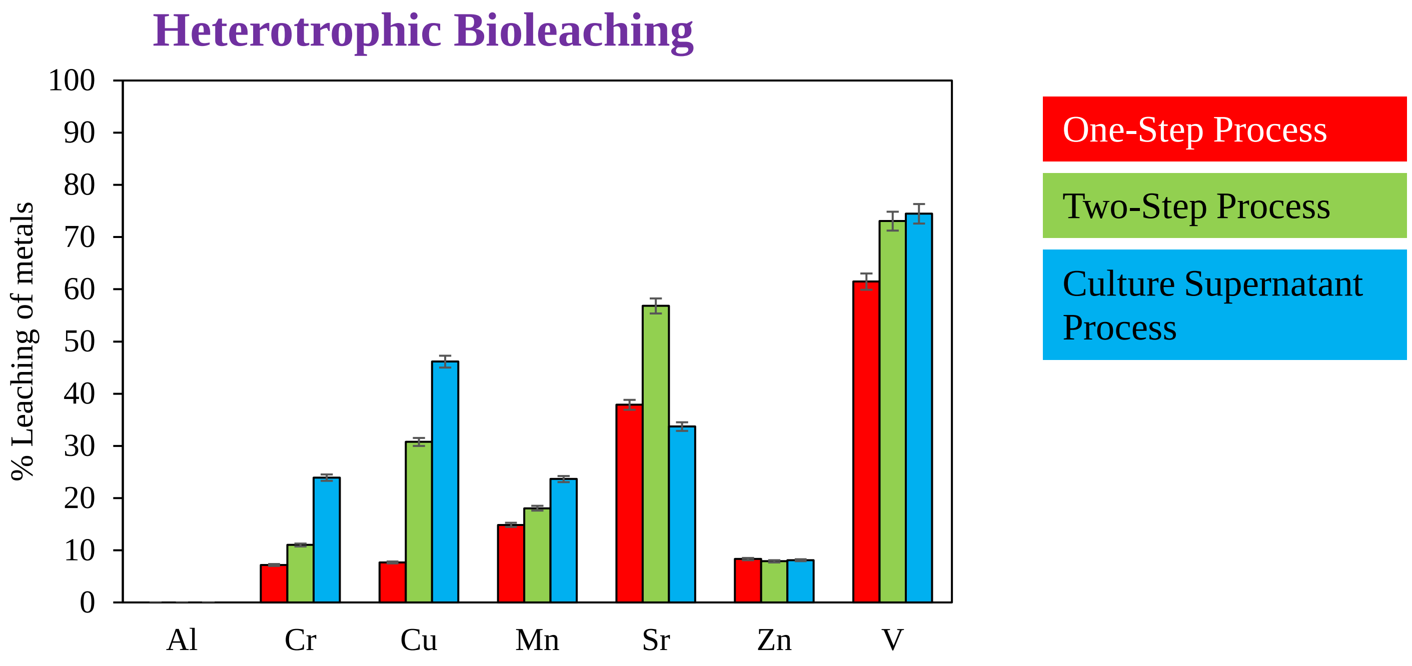
Pseudomonas aeruginosa




Variations of Bioleaching
One-Step Process
Two-Step Process
Culture Supernatant
Culture & Slag is inoculated together
Incubated at optimum conditions
Culture is grown for 24-48 h
Slag is added to grown culture medium
Incubated at optimum conditions
Culture is grown for 24-48 h; Centrifuged and filtered
Slag is added to culture supernatant
Incubated at optimum conditions

Mechanism of Bioleaching: One-step, Two-step and Culture Supernatant Based Bioleaching





- ✓ Acidophilic: Two step bioleaching > Culture supernatant bioleaching > One step bioleaching
- ✓ Along with EPS and acid release, bacteria also plays an important role in leaching
- ✓ Heterotrophic: Culture supernatant bioleaching > Two step bioleaching > One step bioleaching
- ✓ Mostly it is the EPS, surfactant and acid release, which plays the key role in bioleaching

Conclusions

- Iron and steel industry generates huge amount of LD slag, which gets dumped in landfills
- Bioleaching is a more economical and effective method for conversion of insoluble metals to soluble form
- Water washing helped in lowering the pH of slag from 13.44 to 9 and facilitated the bioleaching process
- Bioleaching of all metals were higher for the *Acidithiobacillus ferrooxidans* compared to *Pseudomonas aeruginosa* accept for vanadium
- Even when initial pH was high after slag addition, *Acidithiobacillus ferrooxidans* could lower the pH over time to its optimal pH of about 3
- Both rate and extent of bioleaching was higher for *Acidithiobacillus ferrooxidans*

Conclusions

- Drop in pH with time suggests in-situ production of sulphuric acid using iron from the slag, which also helped in leaching, while increase in sulphate concentration is indicative of conversion of sulphide minerals to sulphates
- In *Pseudomonas* culture, decrease in pH is due to formation of organic acids
- High leaching in the range of 40-70% was observed for Al, Cr, Mn, Sr, V and Zn after 15 days by *Acidithiobacillus ferrooxidans*
- In contrast, for *Pseudomonas aeruginosa*, maximum removal was 51% for V followed by 24% by Sr
- Copper was only leached by the *Pseudomonas* culture
- Mechanism: For acidophilic culture both bacterial interaction as well EPS and enzymes secreted played an important role
- For the heterotrophic culture mostly generation of organic acids, EPS and surfactants were responsible for bioleaching

Acknowledgements

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