Bioleaching

Subjects: Engineering, Chemical

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In bioleaching, the function of the solvent is performed by microorganisms, by the action of either bacteria or fungi, as they participate in the biogeochemical cycle of minerals in direct ways by the metabolism of the microorganisms or indirectly by the products of their metabolism. Therefore, bioleaching is defined as the solubilization of metals from insoluble solid substrates.

biological extraction metals bioprocess bioleaching bacterial bioleaching fungal bioleaching

1. Bioleaching

Leaching is a chemical method for extracting metals of interest [1]. Leaching, peroration, or solid/liquid extraction all involve an operation that consists of extracting with the help of a potentially soluble component a solute that is in solid form accompanied by other undesirable solids [2].

In general, in a leaching process, there are three components:

- A: solid solute that goes into the solution;
- B: inert solid (insoluble in S);
- S: extracting solvent.

In bioleaching, the function of the solvent is performed by microorganisms, by the action of either bacteria or fungi, as they participate in the biogeochemical cycle of minerals in direct ways by the metabolism of the microorganisms or indirectly by the products of their metabolism [3][4].

Therefore, bioleaching is defined as the solubilization of metals from insoluble solid substrates [3]. In the case of employing bacteria, they use the mineral as a substrate, capturing electrons for their metabolic processes and releasing heat and metals without needing any external energy to carry out the process [5]. In the case of fungi, they produce organic acids, which leach metals from solid matrices. Microorganisms can also excrete ligands that stabilize the metal by forming metal-rich complexes [6].

Metal solubilization can be facilitated by biologically produced amino acids, cyanide, and thiosulfate [6]. In addition, microorganisms can participate in the redox cycling of iodine [7], which is a potential alternative leachant for obtaining the metal and decreasing metal solubility by consuming ligands that are bound to the metal or by biosorption, enzymatic reduction, and precipitation, and by employing the metal as a micronutrient, as shown in **Figure 1**.

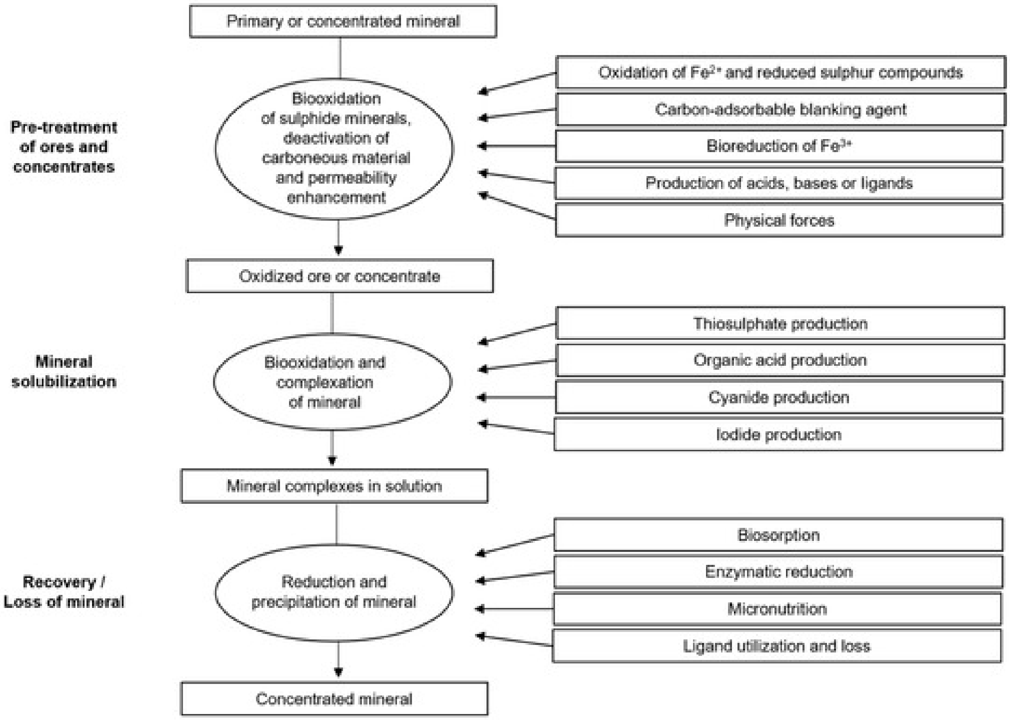

Figure 1. Possible roles of microorganisms in mineral processing and recovery. Source: Adapted with permission from Ref. [6]. 2007, Springer Nature.

As mentioned above, SMMC metal bioleaching processes can be carried out using bacteria or fungi; the decision-making for the selection depends on the objectives to be achieved in the bioprocess. **Table 1** shows the general features for selecting the bacterial or fungal bioleaching application route.

Table 1. General features for the application of bacterial or fungal bioleaching. Source: Authors.

Feature	Bacterial Bioleaching	Fungal Bioleaching
Application	Applied when it is required to recover a metal of interest, and it is not necessary to preserve the properties of the solid matrix	Applied when it is necessary to preserve the properties of the solid matrix, especially the crystalline properties, in case it is a mineral SMMC.
		Applied if the final color of the solid matrix is not of interest.
		Applied if not required to separate the fungus from the solid matrix.
Sterilization and Sanitization	Not required	Required
Stages	Performed in one step	Performed in two steps: Direct method (See Section 4.2).
		Performed in two steps: Indirect method (See Section 4.2).

Feature	Bacterial Bioleaching	Fungal Bioleaching
Operational times	Prolonged due to bacteria acting directly in the process	Direct method: Simultaneous fermentation with leaching can take 3 to 10 days, depending on the target.
	Process times depend on the SMMC/bacteria system	Indirect method: Production of the leaching solvents (fermented broth): can have a production time of 8 to 10 days, with possible constant production and storage for consumption, without this being the limiting stage. The bioleaching process takes approximately 4 to 6 h, depending on the solid matrix and the metal to be extracted.

eserve the properties of the solid matrix. On the other hand, fungal bioleaching is applied when it is necessary to preserve the properties of the solid matrix, especially the crystalline properties, in case it is a mineral SMMC. Furthermore, sterilization and sanitization processes are required in fungal but not bacterial bioleaching due to their resistance to contamination, and because the process is usually performed in one step, which limits the exposure to external contaminants. In contrast, fungal bioleaching is performed in two steps, either by a direct or indirect method.

The operational times differ between the two methods, with bacterial bioleaching being prolonged due to the bacteria acting directly in the process. In contrast, fungal bioleaching has variable times depending on the SMMC/bacteria system and the method used. The indirect method of fungal bioleaching has a longer production time for the leaching solvents (fermented broth) but has a shorter bioleaching process time. The information provided in this table can assist researchers and industry professionals in selecting the appropriate bioleaching method according to their specific metal recovery requirements and constraints.

2. Bacterial Bioleaching

Bacterial leaching, also known as bioleaching, biohydro-metallurgy, or bio-oxidation of sulfides, can be defined as a natural dissolution process resulting from the action of a group of bacteria, mainly of the genus *Thiobacillus*, with the ability to oxidize sulfide SMMC, allowing the release of the metals contained in them [8][9].

Bacterial bioleaching is based on the ability of microorganisms to transform solid compounds into soluble and extractable elements [10] or expose metals contained in ores and concentrates by direct oxidation or indirect chemical oxidation caused by corrosive metabolic by-products generated by electrochemistry, or a combination of both [8].

The attack and solubilization of an SMMC through microorganisms are performed by different mechanisms, which depend on the matrix's sulfur matrix [11][12].

Similarly, the bioleaching process occurs by the catalysis that microorganisms exert during the dissolution of certain SMMC; for example, microorganisms such as bacteria convert metal compounds into their water-soluble forms and are biocatalysts of these leaching processes [13][14]. The microorganism uses SMMC as fuel, electron transfer for its survival purposes, and releasing metals, without the need for external application of energy. In this type of process, high activation energies are not necessary; proof of this is that the reactions take place at low pressure and some at low temperature, depending on the type of microorganism, whereas other ways need extreme conditions for their development and performance [13].

According to Rodríguez et al. (2001), bacterial bioleaching or leaching is understood as the attack and solubilization of an SMMC through the direct or indirect action of different microorganisms [15].

Microorganisms adapted to bioleaching processes are of two categories:

- Autotrophic: These microorganisms obtain nutrients and energy for their life cycles from the inorganic matter surrounding them.
- Heterotrophic: They require the availability of organic matter to complete their life cycles.

In both groups or categories of bacteria, some species operate predominantly in the presence of oxygen. These are the aerobic bacteria that carry out, in the first place, the oxidation reactions and have the property of oxidizing metal sulfides to soluble sulfates. Similarly, anaerobic bacteria can function and carry out their life cycles without oxygen; these batteries first conduct reduction reactions [16]. The respective classification is shown in **Figure 2**.

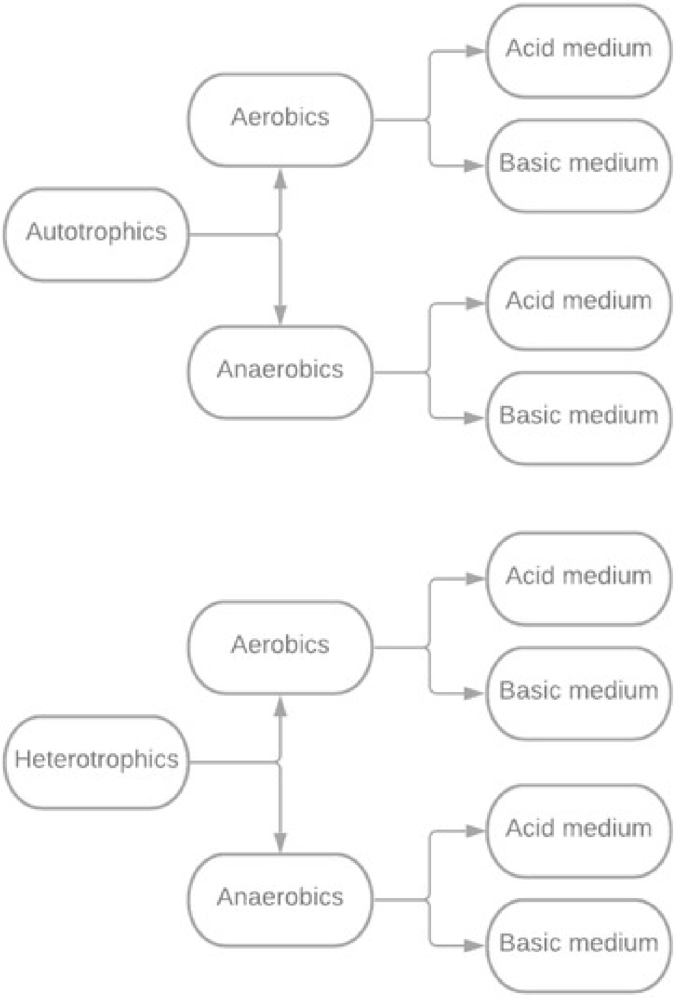

Figure 2. The bacterial classification used in the bioleaching process.

According to **Figure 2**, regardless of the bacterial classification, the main characteristic of the microorganisms used in metal recovery is their capacity to evolve in environments with very aggressive or extreme temperatures, pH, and living conditions [13][15].

Some of the bacteria involved are acidophilic microorganisms capable of surviving at low pH levels, high temperatures, and high concentrations of metallic elements, and whose energy source is the oxidation of Fe^{2+} to Fe^{3+} and reduced sulfur compounds [15].

The most significant area within the biotechnological process of metals is focused on the microbial oxidation of sulfide SMMC. Low pH, high metal concentrations, and sometimes high temperatures characterize the aqueous environments associated with SMMC discharges. However, some microorganisms can live, develop and reproduce under these conditions and in these environments. In these environments, microorganisms use reduced sulfur species and certain metals in solution as a primary energy source, resulting in the solubilization of valuable metals [13][17].

According to Rodriguez et al. (2001), in recovery by bioleaching, the main action of microorganisms is direct oxidation through an enzymatic attack or indirect through regeneration of the leaching agent Fe^{3+} of SMMC [15].

In some cases, the bacteria contribute to the weathering of the gangue by liberating the valuable mineral and facilitating its subsequent attack since the sulfuric acid generated by the bacteria produces a rupture of the Si-O and Al-O bonds in the alumino-silicates of the mineral gangue [15].

The microorganisms used in the leaching of metals from ores and concentrates are presented in **Table 2**. These microorganisms are capable of oxidizing sulfides and sulfur or ferrous iron species. An oxidant (ferric sulfate) is formed when the latter is oxidized.

Table 2. Bacteria used in bioleaching and their optimum conditions.

Microorganism	Energy Source	pH	T (°C)	References
Acidithiobacillus ferrooxidans	Ferrous iron, sulfide minerals, sulfur, thiosulfate	1.7–3.5	28–30	[18]
Leptospirillum ferrooxidans	Ferrous iron	3.0	30	[19]
Acidithiobacillus thiooxidans	Elemental sulfur, thiosulfate	1.0–3.5	28–30	[20]
Thiobacillus thioparus	Elemental sulfur, thiosulfate	7.0–8.5	28–30	[21]
Sulfobacillus thermosulfidoxidans	Ferrous iron, elemental sulfur, sulfide minerals	2.1–2.5	50–55	[22]
Sulfolobus acidocaldarius	Elemental sulfur, yeast extract	2.0–3.0	70–75	[23]
Sulfolobus brierly	Elemental sulfur, ferrous iron, yeast extract	2.0–3.0	60	[24]
Acidiphilium acidophilum	Elemental sulfur, thiosulfate, yeast extract, salts, sugars, amino acids	2.0–3.0	28–30	[24]

The bioleaching of *A. thiooxidans* and *A. ferrooxidans* contributes via both “contact” and “non-contact” mechanisms. The “contact” mechanism considers that most cells adhere to the surface of the bioleaching substrates. The “non-contact” mechanism is related to redox reactions, such as iron (III) reduction and sulfur oxidation [17][25].

In this sense, there are many and varied definitions of bioleaching. However, what should be made clear is that this leaching can be determined because the raw material studied can be under the direct or indirect action of microorganisms [26].

According to **Table 2**, a direct mechanism is understood as that which is mediated by bacterial action and where the chemical reactions are catalyzed enzymatically; this option also supposes the physical contact of the microorganisms with the solid matrix [26].

On the other hand, an indirect mechanism involves chemical reactions, enzymatic or non-enzymatic, with no physical contact between the microorganisms and the solid matrix. However, the microorganisms are relevant in forming chemical reagents that can participate in the process [26][27].

The first attempt to explain the mechanism of bioleaching was made by Silverman and Ehrlich in 1964 when they proposed two possible mechanisms [28], as shown in **Figure 3**.

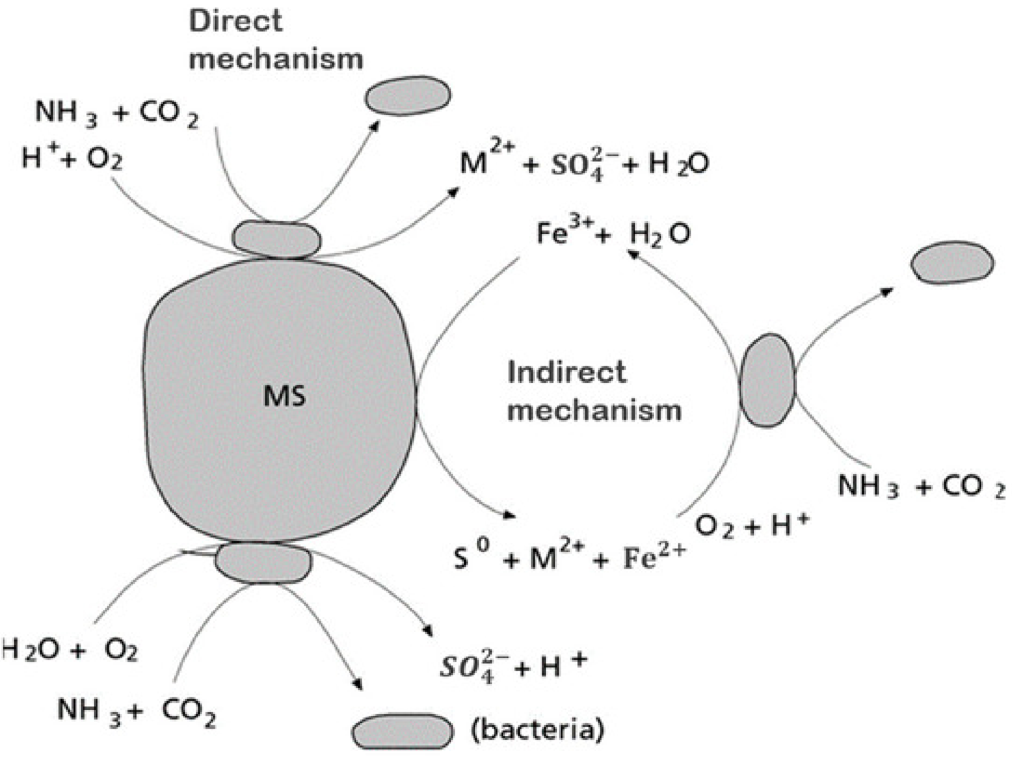

Figure 3. Direct and indirect mechanisms of bioleaching. Adapted from [28].

According to the first possible mechanism, the bacteria attack the metal sulfide directly by adhering to the mineral surface and then enzymatically oxidize it by transporting electrons from the reduced part of the mineral, usually a sulfide, to dissolved oxygen. The general reaction is presented in Equations (1) and (2) [4][10][14].

$$MS + 2O_2 \rightarrow M^{2+} + SO_4^{2-}. \quad (1)$$

In the case of pyrite, the above reaction would look like this:

$$FeS_2 + {}^{7}\!/_{2}O_2 + H_2O \xrightarrow{Bacteria} Fe^{2+} + 2SO_4^{2-} + 2H^+. \quad (2)$$

The first mechanism proposed (Equation (1)) states that the oxidation of the mineral is carried out by direct enzymatic action, in which the role of the microorganisms is to catalyze the metal sulfide dissolution reaction. The iron-oxidizing bacteria can leach metal sulfides directly without the participation of biologically produced ferric sulfate. The M represents a bivalent metal. The second mechanism, called indirect (Equation (2)), is based on microorganisms oxidizing the minerals by generating ferric ion. In the case of pyrite, the direct transformation of sulfide to sulfate occurs through enzymatic oxidation, where the ferrous sulfate formed is oxidized to ferric sulfate in a later stage by the bacteria [19].

This theory of direct mechanism has been supported by several experimental studies that confirm the adherence of bioleaching bacteria to the surface of minerals. The work presented by Berry and Murr evidence that *Acidithiobacillius* spp. secrete some substances that can help the attack, although their nature is unknown [29].

Similarly, pyrite crystals exposed to the action of *A. ferrooxidans* were observed under the scanning electron microscope, detecting traces of corrosion in the crystals and suggesting that the bacteria caused these through a metabolite that could act in three different ways: oxidation of the ferrous ion to ferric, solubilization of the sulfur on the surface of the mineral or by direct attack. In addition, it was found that *A. ferrooxidans* could discern the most favorable regions of the mineral surface to obtain its energy source and select the site of attack according to the best availability of nutrients. However, the authors, far from using these results in favor of the direct mechanism, have used them to explain the indirect mechanism known as contact leaching [30].

Studies carried out by different authors also detected by electron microscopy the formation of holes on the surface of dissolved sphalerite in the presence of bacteria, and it was concluded that they occurred due to the direct attack of the bacteria on the surface of the mineral [31]. Tributsch studied by SEM the surface of lead sulfide after bacterial attack, showing depressions where the bacteria had been located. This author concluded that the bacteria produced a chemical carrier that promoted the attack at the point of adhesion of the microorganisms [32].

Studies by some authors mention that bacteria breathe using minerals, which provides a new vision of the problem, although, in this case, not related to sulfide minerals [33][34].

In contrast to the direct mechanism, the indirect mechanism considers the action of ferric ions on the sulfide ore dissolving it. Through this chemical leaching reaction, ferrous ions and elemental sulfur are produced. Finally, these chemical species are biologically oxidized to ferric iron and sulfate ions. This mechanism, in principle, does not require the adherence of cells to the sulfide mineral [26][34].

Some of the bacteria mentioned in **Table 3** show extraction efficiencies in laboratory experiments with SMMC, such as minerals, sediments contaminated with metals after wastewater treatment, and printed circuit boards, among other materials that can be returned to the production chain once they fulfill their useful life and become waste.

Table 3. Bacterial bioleaching: operating conditions and metal extraction efficiencies of different SMMCs.

Microorganism	SMMC	Metal	pH	T (°C)	Agitation	Pulp Density	Efficiencies	References
A. ferrooxidans, *Desulfotomaculum geothermicum*	Crushed and screened graphitic schist with a diameter of 8 mm	Iron, zinc, nickel, copper, and cobalt	1.7–2.0	40–50	-	-	In 500 days, the recoveries were Ni 92%, Zn 82%, Co 14%, and Cu 2%.	[35]
A. ferrooxidans	Pyrrhotite, chalcopyrite and arsenopyrite	Iron, copper	2.8–3.2	–	-	-	In 41 days, recoveries were 47.4 mg/L at a pH of 3.2.	[36]
A. ferrooxidans	Dried and crushed sludge at different particle sizes	Gold, copper, zinc, lead	1.8–2.2	30	100 rpm	6.0% (*w*/*v*)	In 14 days, the extractions were 4.71%, 9.01% Pb, 12.98% Cu, and 31.88% Zn.	[25]
A. ferrooxidans	Quartz, chlorite, chalcopyrite, albite, pyrite	Aluminum, iron, copper	1.8	30	150 rpm	-	In 5 weeks, metal recoveries were 47.29% Al, 54.41% Fe, and 28.08% Cu.	[37]
A. ferrooxidans FT-22, *A. ferrooxidans* FT-23, *A. ferrooxidans* BF, and *A. ferrivorans*	Albite, quartz, clinochlore, muscovite, illite	Silver, copper	10.5–11.0	25	20–30 rpm	40% (*w*/*v*)	In 48 h, the recovery of metals was 51% Ag and 70% Cu.	[38]
Sulfobacillus thermosulfidooxidans, *A. thiooxidans*, *Acidiphilum multivorum*, and *Leptospirillum Ferriphilum*.	Chalcopyrite	Iron, copper	2.0	30	-	1–6% (*w*/*v*)	In 11 days, the metal recovery was 28.57% Fe and 39.55% Cu.	[39]
S. Thermosulfidooxidans, *A. thiooxidans*/*A. ferrooxidans*, *S. thermotolerans*, and *A. albertensis*.	Clay, sand, silt	Zinc, copper, nickel, chromium	1.5–3.1	30	200 rpm	10% (*w*/*v*)	In 20 days of operation, metal recovery was 49% Zn, 50% Cu,	[40]

Microorganism	SMMC	Metal	pH	T (°C)	Agitation	Pulp Density	Efficiencies	References
							65% Ni and 27% Cr.	
Sulfobacillus thermophidus oxidans	Printed circuit board (PCB)	Aluminum, lead, zinc, and tin	-	45	120–145 rpm	0.33% (*w*/*v*)	Recovery of 83% Zn, 89% Cu, and 81% Ni in 18 days.	[41]
A. thiooxidans and *A. ferrooxidans*	Soil contaminated with metals and metalloids	Cadmium, copper, lead, zinc, zinc, chromium, iron	5.6	30	150 rpm	10% (*w*/*v*)	In 42 days, metal recovery was 36% Fe and 70% Zn.	[42]
Burkholderia spp. Z-90	Soil contaminated with metals and metalloids	Cadmium, arsenic, copper, lead, lead, zinc, chromium, iron	3.0	35	180 rpm	5% (*w*/*v*)	In 5 days, the maximum metal recovery achieved was 31.6% As, 37.7% Cd, 24.1% Cu, 52.2% Mn, 32.5% Pb, and 44% Zn.	[43]
Shewanella putrefaciens	Soil contaminated with metals and metalloids	Cadmium, arsenic, copper, lead, lead, zinc, chromium, iron	2.2	30	100 rpm	3% (*w*/*v*)	Arsenic recovery was 57.5% in 40 days.	[44]
Acidithiobacillus, *Acetobacter*, *Acidophilum*, *Acidophilum*, *Arthrobacter* spp., and *Pseudomonas* spp.	Panchakavya (soil mixture)	Cadmium, arsenic, copper, lead, lead, zinc, chromium, iron	2.6	30	120–180 rpm	0.2–1% (*w*/*v*)	Metal recovery in 5 days was 64% Pb and 49% Cu.	[45]
Massilia spp., *Alicyclobacillus* spp., and *Micromonospora* spp.	Soil contaminated with metals and metalloids	Cadmium, arsenic, copper, lead, lead, zinc, chromium, iron	3.5	30	180 rpm	1% (*w*/*v*)	The metal extraction in 10 min was 32.09% Cd	[46]

Microorganism	**SMMC**	**Metal**	**pH**	**T (°C)**	**Agitation**	**Pulp Density**	**Efficiencies**	**References**
Myxotrophic acidophiles	Soil contaminated with metals and metalloids	Cadmium, arsenic, copper, lead, lead, zinc, chromium, iron	2.0	25	175 rpm	4% (*w*/*v*)	In 14 days, the two-step bioleaching achieved the extraction of 34% Cd	[47]
Indigenous bacteria	Agricultural land	Zinc, copper, nickel	8.0	28	180 rpm	1% (*w*/*v*)	In 9 days, the maximum metal extraction achieved was 74.72% Cu, 35.35% Ni, and 69.92% Zn.	[48]
A. ferrooxidans, *A. thiooxidans*, and *L. ferriphilum*	Pyrite and sulfosalts	Aluminum, manganese, iron, copper, zinc, mercury, zinc, mercury	4.0	30	180 rpm	5% (*w*/*v*)	In 31 days, the maximum metal recovery was 93.3% Cu, 92.13% Mn, and 96.1% Zn.	[49]
Sulfobacillus thermosulfidooxides and *A. caldus*	Pyrite and sulfosalts	Aluminum, manganese, iron, copper, zinc, mercury, zinc, mercury	7.5	45	180 rpm	5% (*w*/*v*)	Fermentation was carried out for 31 days, and the metal recovery efficiency was 45% As, 89% Cd, 94% Cu, 34% Hg, 95% Mn, and 98% Zn.	[49]
Indigenous bacteria	Port sediments	Copper, chromium, cadmium, lead, zinc	6.0	30	100 rpm	1% (*w*/*v*)	During 30 days of processing, the recovery of metals was 29% Cu, 8% Ni, 5% Pb, and 39% Zn.	[50]

Microorganism	SMMC	Metal	pH	T (°C)	Agitation	Pulp Density	Efficiencies	References
Bacteria from exogenous soil	Port sediments	Copper, chromium, cadmium, lead, zinc	8.0	30	100 rpm	4% (*w*/*v*)	During 30 days of processing, the recovery of metals was 100% Cu, 95% Cr, 100% Ni, 100% Pb, 100% Zn, 100% Cu, 95% Cr, 100% Ni, 100% Ni, 100% Pb, 100% Pb and 100% Zn.	[50]
A. ferrooxidans and *A. thiooxidans*	Anaerobic sediment from urban wastewater	Copper, chromium, cadmium, lead, zinc	5.0	25	120 rpm	15% (*w*/*v*)	Metal recovery during 57 days was 43% Cu and 80% Zn.	[51]
A. ferrooxidans, *A. thiooxidans*, and *Leptospirillum ferriphilum*	Sediment from sewage outfall	Copper, chromium, cadmium, lead, zinc	4.0	30	180 rpm	5% (*w*/*v*)	Metal recovery was 90.9% Cu and 94.74% Zn; elements such as Cd, Hg, Mn, and Pb were below 30%.	[52]
A. ferrooxidans	Mining tailings	Copper, iron, cadmium, antimony, zinc, nickel, chromium, nickel, chromium	3.0	30	200 rpm	5% (*w*/*v*)	In 20 days, the maximum efficiency achieved was 36.2% Cu, 65.95% Cr, 97.4% Ni, 2.2% Sb, and 34.8% Zn.	[53]
A. ferrooxidans and *A. thiooxidans*	Mining tailings	Arsenic, zinc, copper, lead	2.5	30	200 rpm	5% (*w*/*v*)	Metal recovery in 25 days was 72.2% As, 47.1% Cu, 99.5% Mn,	[53]

Microorganism	SMMC	Metal	pH	T (°C)	Agitation	Pulp Density	Efficiencies	References
							and 78.9% Zn.	
A. ferrooxidans	Mining tailings	Arsenic, zinc, copper, lead	2.0	30	200 rpm	20% (*w*/*v*)	The maximum metal recovery achieved in 50 days was 71.37% Fe, 0.82% Pb, and 97.38% Zn.	[54][55]
A. thiooxidans	Tailings from an abandoned and inactive mine	Arsenic, zinc, copper, lead	1.8	40	150 rpm	0.5% (*w*/*v*)	Arsenic recovery in 25 days was 47%.	[53][56][57]
A. ferrooxidans	Mine and metallurgical wastes	Lead, iron, copper, zinc	1.5	40	160 rpm	20% (*w*/*v*)	In 50 days of fermentation, the metal recovery achieved was 85.45% Fe, 4.12% Pb, and 97.85% Zn.	[54][55]
A. ferrooxidans and *A. thiooxidans*	Mine tailings deposits	Silver, lead, mercury, zinc, zinc, arsenic, manganese, indium, gallium, germanium, cobalt	6.0	30	200 rpm	5% (*w*/*v*)	In 20.8 days, 42.4% As, 45% Cu, 47.7% Fe, 92% Mn, and 67.2% Zn were extracted.	[53][56]
A. ferrooxidans and *A. thiooxidans*	Mine waste	Arsenic, manganese	2.5	30	200 rpm	5% (*w*/*v*)	In 35 days, metal recovery was 96.7% As and 100% Mn.	[20]
Leptospirillum ferriphilum, *A. caldus*, *Sulfobacillus thermosulfidooxidan*, *A. sulfuroxidans*, *Ferroplasma acidiphilum*,	Mining waste materials	Silver, lead mercury, zinc, arsenic, manganese, indium, gallium,	1.7	45	150 rpm	5% (*w*/*v*)	Bioleaching was carried out for 50 days, and the efficiency of recovered metals was	[58]

Microorganism	SMMC	Metal	pH	T (°C)	Agitation	Pulp Density	Efficiencies	References
Acidiplasma sp., *Sulfobacillus acidophilus*, *Acidithiobacillus* spp., and *Acidiphilum cryptum*.		germanium, and cobalt.					90% Cu and 99% Zn.	
Leptospirillum ferriphilum, *A. caldus*, *Sulfobacillus* sp. and *Ferroplasma* sp.	Mine tailings deposits	Silver, lead, mercury, zinc, zinc, arsenic, manganese, indium, gallium, germanium, cobalt	1.8	45	150 rpm	5% (*w*/*v*)	In 30 days, the metal recovery was 59.5% Co, 55% Cu, and 98.2% Ni.	[59]
Leptospirillum ferriphilum, *A. caldus*, *Sulfobacillus* sp. *and Ferroplasma* sp.	Mine tailings deposits	Silver, lead, mercury, zinc, zinc, arsenic, manganese, indium, gallium, germanium, cobalt	1.2	45	150 rpm	5% (*w*/*v*)	In 30 days, the metal recovery was 36.5% Co, 72% Cu, and 61.2% Ni.	[59]
A. caldus, *Leptospirillum ferriphilum*, *Methylophaga* spp. and *Sphingomonas* spp.	Tailing material in mining areas in Germany	Silver, lead, mercury, zinc, zinc, arsenic, manganese, indium, gallium, germanium, cobalt	1.5	40	550 rpm Aeration: 5 L/min	15% (*w*/*v*)	Fermentation was carried out for seven days, and the metal extraction achieved was 105,000 mg/kg.	[18]
A. caldus and *Leptospirillum ferriphilum*	Scorodite [66]	Arsenic, copper, iron, sulfur	1.2	45	Aeration: 200 mL/min	1% (*w*/*v*)	The maximum recovery achieved during 88 days was 97% As.	[60]
Acidophilic ferrous, iron-oxidizing, and sulfur-oxidizing species	Tailing material in mining areas in Germany	Silver, lead, mercury, zinc, zinc, arsenic, manganese, indium, gallium, germanium,	1.6	30	100 rpm	4% (*w*/*v*)	During 22 days, the extraction [68] efficiencies reported were 100% As, 85% Cd, 40% Cu.	[61]

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Fungi	Organic Acids
Yarrowia lipolytica	Citric acid
Mucor spp.	Fumaric and gluconic acid
Rhizopus spp.	Lactic, fumaric and gluconic acid
Aspergillus niger	Citric, oxalic and gluconic acids

Fungi	**Organic Acids**
Aspergillus spp.	Citric, malic, tartaric, ketoglutaric, itaconic and aconitic acid
Penicillium spp.	Citric, malic, tartaric, ketoglutaric, ketoglutaric and gluconic acids
Schizophyllum commune	Malic acid
Paecilomyces variotii	Malic acid

iron-oxidizing and sulfur-oxidizing species	material in mining areas in Germany	manganese, indium, gallium, germanium, cobalt	1.8	30	100 rpm	4% (*w*/*v*)	extraction efficiencies were 79.9% In and 94.6% Zn.	[61]
Acidophilic ferrous iron-oxidizing and sulfur-oxidizing species	[69] Tailing material in mining areas in Germany	Silver, lead, mercury, zinc, zinc, arsenic, manganese, indium gallium, germanium, cobalt	1.8	30	100 rpm	10% (*w*/*v*)	During 22 days, the reported extraction efficiencies were 72% As, 88% Cd, 87% In, and 81% Zn.	[61]
A. thiooxidans Ram 8, *A. ferrooxidans* Ram 6F, *Leptospirillum ferrooxidans*, and *Ferroplasma acidiphilum* BRGM 4	Tailing and mining residues (pyrite, quartz, etc.)	Iron, zinc, silica, cobalt, cobalt, nickel, aluminum, manganese, arsenic	2.0 [68]	30	150 rpm	10% (*w*/*v*)	The recovery achieved in the fermentative process was 91% Co, 57% Cu.	[62]
Marinobacter sp., *Acidithiobacillus* spp., *Leptospirillum* sp., *Cuniculiplasma* sp., *Nitrosotenius* sp. and *Ferroplasma* sp.	Tailing and mining residues (pyrite, quartz, etc.)	Iron, zinc, silica, cobalt, cobalt, nickel, aluminum, manganese, arsenic [68][72][73][74]	1.5	30	300 rpm	10% (*w*/*v*)	In 10 days of retention, the amount of metal recovered was 87% Co, 43% Cu, 67% Ni, and 100% Zn.	[63]
Leptospirillum ferriphilum YSK, *Ferroplasma thermophilum* L1, *A. caldus* S1, and *A. thiooxidans* A01.	Metallurgical industry [75] waste	Copper, cobalt, nickel, zinc	1.8	40	175 rpm	5% (*w*/*v*)	In 16 days, the maximum copper recovery was 58.7% [75][76]	[64]
Indigenous bacterial and fungal strains	Mining waste	Silver, manganese	2.0	30	200 rpm	6% (*w*/*v*)	67% Ag, 745 Mn.	[65]

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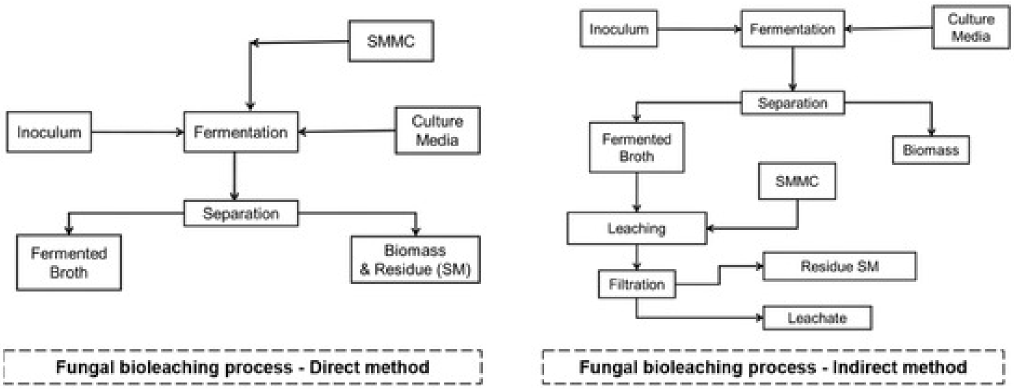

Figure 4. Fungal bioleaching process. Source: the authors.

Direct method: this method is carried out in one stage where the fermentation occurs: SMMC/culture medium/inoculum (fungus) simultaneously. In the process, the fungus produces the leaching substances, mainly organic acids, and simultaneously extracts the metal contained in the SMMC. The process can take 3 to 10 days depending on the objective, and the pH value of the fermentation usually starts between 6 and 7. As the bioprocess progresses, it reaches pH values between 3.5 and 4, which leads to a decrease in the efficiency of the process because the fungus is inhibited by the presence of SMMC residues [68].

Indirect method: this approach is carried out in two stages [68].

Stage 1: Production of the solvent extractor or fermented broth. Fermentation: culture medium/inoculum (fungus) for 8–10 days. Subsequently, a separation process is carried out, where the biomass is discarded, and the focus is on the fermented broth. This stage generally presents pH values below 3.0.

Stage 2: The fermented broth is in contact with the SMMC, a process that can take 4 to 8 h depending on the SMMC. Subsequently, a separation process is carried out, where the metal-free solid residues are discarded and the focus is on the fermented broth containing the extracted metals (leachates).

Acids are excellent metal leachants from SMMC. Heterotrophic metabolism can also achieve leaching due to the excretion of siderophores and organic acids. These provide protons and metal complexing anions, as citrate and oxalate anions can form stable complexes with many metals [68], including chelates which are relevant in metal dissolution by acidolysis and complex formation mechanisms. In conclusion, the main mechanisms through which organic acids interact with metals (bioleaching reactions) are acidolysis (acid-base reaction), redoxolysis, bioaccumulation, chelates, and complex formation mechanisms [3].

The efficiency of the process depends on the acids produced and their acidity depending on their functional group (e.g., carboxylic or sulfonic). Considering that these acids are not equal in the number of carboxylic groups, hydroxyl groups, and carbon–carbon double bonds in their molecules, they are classified according to their typical characteristics of the carbon chain, saturation, substitution, and functional groups.

Based on the Lewis acid-base theory, the ability to release protons is shown by the strength of the acid. The stronger the acidity, the stronger the ability to release protons. For example, oxalic acid (pKa 1.23) shows higher acidic capacity than formic acid (pKa 3.75), implying that the former has higher leaching power provided that the conjugate base of the oxalate anion does not interact strongly with the metal of interest, causing the precipitation of metal complexes [79].

Studies show that oxalic acid (pKa 1.23) leached more iron ions than lactic acid (pKa 3.86). The pKa values of each carboxylic acid indicate that oxalic acid is stronger than lactic acid, which leaches metals more efficiently. In addition, the complexation reaction and the formation of iron oxalates may play a relevant role in increasing the leaching of iron ions, which is confirmed in the leaching of iron contained in kaolin using oxalic acid, which is more effective than when organic acids such as citric, malonic, or acetic acid are used [80]. Oxalates are known for chelating metals, and this can be exploited for the dissolution and separation of metals. The increase in the solubility of simple oxalate compounds in the presence of excess oxalate provides the basis for formation of the oxalate complex [81].

Metallic oxalates display a diverse range of solubilities which are influenced by the particular metal cation and solution conditions. Insoluble oxalates include calcium oxalate (CaC_2O_4), silver oxalate ($Ag_2C_2O_4$), and lead oxalate (PbC_2O_4). Conversely, sodium oxalate ($Na_2C_2O_4$) and potassium oxalate ($K_2C_2O_4$) exhibit high solubility, while barium oxalate (BaC_2O_4) is generally soluble. Transition metal oxalates like iron oxalate (FeC_2O_4) and nickel oxalate (NiC_2O_4) can display variable solubility depending on conditions. Factors such as pH, temperature, presence of other ions, and ligand complexation influence the solubility behavior of metallic oxalates [81].

In bioleaching processes, the binding behavior of oxalic acid is influenced by adsorption of oxalic acid onto metal surface which leads to the formation of an upright mono-oxalate species, with the carboxylate group binding to the surface. This upright orientation enables interactions between the carboxylic acid group and the surrounding environment, resulting in the creation of a chemically functionalized surface. The presence or absence of intramolecular hydrogen bonding determines the various surface species of mono-oxalate. The tilting of the molecules is influenced by surface coverage and temperature, leading to the observation of both unidentate and bridging species [82].

L-aspartic acid can release a total of three protons: two protons from its carboxyl groups and one proton from its amino group. On the other hand, L-tartaric acid does not possess an amino group, and therefore, two acidity constants are reported specifically for its carboxyl groups. In the case of L-glutamic acid, two protons are released from its carboxyl groups, while an additional proton is released from its amino group. Glutamate and aspartate chelate metal ions weakly via the amino nitrogen and carbonyl oxygen bind. A stronger chelation occurs upon amide-nitrogen-bound hydrogen by some metal ions such as Cu^{2+}. This reaction occurs in neutral pH conditions ($pH \approx 7$) with Cu^{2+} [83].

Several reports have documented the leaching of metals with fungi. Fungi of the genera *Aspergillus* and *Penicillium* are among the most effective and relevant for biological leaching due to filamentous fungi’s robust adaptability and ability to tolerate metal contamination stress [3].

Laboratory studies have been carried out using fungi, where only the leaching action is specified according to the type and species of microorganism. For example, *A. niger*, *P. simplicissimum*, and *P. purpurogenum* are related to the production of low-molecular-weight metabolites, mainly organic acids such as gluconic acid, pyruvic acid, citric acid, oxalic acid, malic acid, and succinic acid, different from the mechanism reported for *R. rubra*, *A. thiooxidans* and *A. ferrooxidans* [68].

Some of the most common organisms for fungal bioleaching are the genera *Acidithiobacillus*, *Aspergillus*, and *Penicillium*. For example, *Penicillium simplicissimum* is used to extract elemental Zn from ZnO. Fungi are also particularly suitable for phosphorus bioleaching, where organic acids such as citric and oxalic acid solubilize P from Fe and Al phosphates. In this process, carboxylic anions compete with binding sites that chelate Al^{3+} and Fe^{3+} [67].

Many microorganisms are reported to solubilize metals in soils, including *Aspergillus niger*, *Penicillium purpurogenum*, *Rhodotorula rubra*, *Acidithiobacillus thiooxidans*, and *Acidithiobacillus ferrooxidans*. The mechanism of metal solubilization during the process is related to a chemical process where the binding of microorganisms to the mineral can enhance dissolution [14][84].

Despite successful records of fungal tolerance to metals at the laboratory scale, no documentation of their use at the industrial scale is available [3][85].

In **Table 5**, fungal bioleaching experiments are presented: operating conditions and metal extraction efficiencies of different SMMC.

Table 5. Fungal bioleaching: operating conditions and metal extraction efficiencies of different SMMCs.

Microorganism	SMMC	Metal	pH	T (°C)	Agitation-Aeration	Pulp Density	Result	References
Aspergillus niger	Spent FCC catalyst (zeolites), crushed and screened	Nickel, vanadium, aluminum, aluminum, antimony, molybdenum, cobalt, tungsten	6.0	30	-	1% (*w*/*v*)	In 60 days, the recovery was 9% Ni, 23% Fe, 30% Al, 36% V, and 64% Sb.	[86]
Penicillium simplicissimum	Spent FCC catalyst (zeolites), crushed and screened	Nickel, vanadium, aluminum, aluminum, antimony, molybdenum, cobalt, tungsten	4–7	30	-	3% (*w*/*v*)	In two-step bioleaching, 32% Al, 67% Co, 65% Mo, and 38% Ni were recovered in 30 days.	[87]
Purpureocillium lilacinum y Aspergillus niger (7:3)	Printed circuit boards, crushed with d < 40mm	Aluminum, lead, zinc, and tin	5.0	30	150 rpm	3 to 8% (*w*/*v*)	In 27 days, 15.7 ± 0.87% Al, 20.5 ± 0.78% Pb, 49.5 ± 0.38% Zn and 8.1 ± 0.34% Sn were extracted.	[88]
Aspergillus niger	Printed circuit boards, shredded and screened	Aluminum, lead, zinc, copper	5.08	25	120 rpm	3.9% (*w*/*v*)	In 21 days, the maximum recovery of metals was 98.57% Zn, 43.95% Ni, and 64.03% Cu.	[89]

Microorganism	SMMC	Metal	pH	T (°C)	Agitation-Aeration	Pulp Density	Result	References
P. simplicissimum	Printed circuit boards	Aluminum, lead, zinc, copper	6.0	30	100–400 mL/min	1–10% (*w*/*v*)	The maximum recovery achieved for Cu and Ni was 40% in 7 days.	[90]
Aspergillus niger	Saprolite	Iron, silica, nickel, manganese	5.0	95	400 rpm	10% (*w*/*v*)	The maximum recovery achieved in 24h was 65% Ni and 58% Fe.	[91]
Aspergillus niger	Limonite	Iron, aluminum, silica, manganese	5.0	95	400 rpm	10% (*w*/*v*)	Maximum recovery achieved in 24h was 78% Ni and 60% Fe.	[91]
Penicillium simplicissimum	Waste ash from power plant	Vanadium, iron, nickel	4.5	30	130 rpm	1% (*w*/*v*)	The maximum extraction achieved was 48.3% Fe, 19% V, and 12% Ni in 15 days.	[92]
Aspergillus niger NCIM 548	Chromite	Nickel, cobalt	2.5	30	150 rpm	2% (*w*/*v*)	In 21 days of fermentation, the metal recovery was 70.49% Ni and 66.93% Co.	[93]
Aspergillus niger	Fly ash from municipal solid waste incinerators	Aluminum, lead, zinc, copper	10–12	30	120 rpm	1–8% (*w*/*v*)	After 30 days, the recovery of Cu, Pb, and Fe metals was between 60 to 70%, 55 to 70%, and 30 to 40%, respectively.	[94]
Aspergillus niger y Aspergillus tubingensis	Electronic waste (e-waste)	Copper, lead, tin, silver, gold, platinum, platinum, aluminum, manganese, and palladium	5.0	30	140 rpm	1% (*w*/*v*)	The achieved metal recovery was 80% Al, 50% Co, 90% Mn, 80% Li and 67% Ni in 27 days.	[95]
Aspergillus niger	Bauxite (d < 180 µm)	Aluminum, iron, silica	6.5	30	130 rpm	1% (*w*/*v*)	Metal recovery in 10 days was 82.80% Al.	[96]

Microorganism	SMMC	Metal	pH	T (°C)	Agitation-Aeration	Pulp Density	Result	References
Aspergillus niger adaptado	Lithium-ion batteries (LIBs)	Cobalt, lithium, nickel, manganese, copper, aluminum, graphite, and other materials	5.4	30	120–170 rpm	0.3–1% (*w*/*v*)	The obtained recovery efficiency from spent LIBs was 100%, 94%, 72%, 62%, 45%, and 38% for Li, Cu, Mn, Al, Ni, and Co, respectively, in 27 days.	[97]
Penicillium chrysogenum strain F1	Soil contaminated with metals and metalloids	Cadmium, copper, lead, zinc	-	25	120 rpm	5% (*w*/*v*)	In 15 days, the recovery of metals was 50% Cd, 35% Cu, 9% Pb, and 40% Zn.	[84]
Phanerochaete chrysosporium	Waste of electrical and electronic equipment	Copper, lead, tin, silver, gold, platinum, platinum, aluminum, manganese, and palladium	5.0	30	150 rpm	1% (*w*/*v*)	In 14 days, the copper recovery achieved was 54%.	[79]
Aspergillus fumigatus (M3Ai)	Soil contaminated with metals and metalloids	Cadmium, copper, lead, lead, zinc, chromium	6.5	30	130 rpm	5% (*w*/*v*)	In 3 days, the metal recovery in two-step bioleaching was 79% Cd and 69% Cr.	[98]
Aspergillus flavus	Soil contaminated with metals and metalloids	Cadmium, copper, lead, lead, zinc, chromium	-	30	130 rpm	5% (*w*/*v*)	In 15 days, the maximum metal recovery was 39.77% Cd, 18.16% Pb, and 58.22% Zn.	[50]
Fibroporia vaillantii	Wood preservative: Chromated copper arsenate	Chromium, copper, arsenic	3.1	30	150 rpm	-	In 28 days of fermentation, the maximum metal recovery efficiency was 87% Cu, 80% Cr, and 100% As.	[99]
Geotrichum sp. *G1 y Bacillus* sp. *B2*	Soil contaminated	Cadmium, copper, lead,	2.0–10	-	-	2%	Chromium extraction at 28	[100]

Microorganism	SMMC	Metal	pH	T (°C)	Agitation-Aeration	Pulp Density	Result	References
	with metals and metalloids	lead, zinc, chromium					days was 94.8%.	
Aspergillus niger (*M1DGR*)	Soil contaminated with metals and metalloids	Cadmium, copper, lead, lead, zinc, chromium	6.5	30	130 rpm	5% (*w*/*v*)	The 3-day two-step bioleaching metal recovery was 98% Cd and 43% Cr.	[98]
Penicillium rubens (*M2Aiii*)	Soil contaminated with metals and metalloids	Cadmium, copper, lead, lead, zinc, chromium	6.5	30	130 rpm	5% (*w*/*v*)	The 3-day metal recovery in two-step bioleaching was 79% Cd and 69% Cr.	[98]
Penicillium, *Aspergillus*, *y Fusarium*	Panchakavya (soil mixture)	Cadmium, arsenic, copper, lead, lead, zinc, chromium, iron	2.6	30	120–180 rpm	0.2–1% (*w*/*v*)	The 5-day metal recovery was 64% Pb and 49% Cu.	[45]
Aspergillus niger strain SY1	Contaminated sediment	Cadmium, arsenic, copper, lead, lead, zinc, chromium, iron	6.5	30	220 rpm	10% (*w*/*v*)	Metal recovery in 7 days was 93.5% Cd, 62.3% Cu, 11.5% Pb, and 68% Zn.	[101]
Aspergillus niger strain SY1	Contaminated sediment	Cadmium, copper, lead, lead, zinc, chromium	6.5	30	220 rpm	2.5% (*w*/*v*)	In 15 days of fermentation, the recovery efficiency achieved was 90% Cd, 20% Pb, 60% Cu, and 60% Zn.	[101]
Penicillium chrysogenum strain KBS3	Mine tailings	Cobalt, zinc, copper, nickel, manganese, lead	2.5	30	120 rpm	10% (*w*/*v*)	In 25 days, the maximum metal recovery achieved was 60% Co, 67% Cu, 69% Mg, 55% Ni, and 65% Zn.	[65]
Aspergillus fumigatus	Mine tailings	Arsenic, iron, manganese, lead, zinc, zinc	5.0	30	150 rpm	8% (*w*/*v*)	In 40 days, the one-step bioleaching recovered 62.1% As, 58.4% Fe,	[102]

Microorganism	SMMC	Metal	pH	T (°C)	Agitation-Aeration	Pulp Density	Result	References
							100% Mn, 56.1 Pb, and 54.43% Zn.	
Aspergillus fumigatus	Mine tailings	Arsenic, iron, manganese, lead, zinc, zinc	5.0	30	150 rpm	8% (*w*/*v*)	The two-step bioleaching showed that the maximum metal recovery would be 32% As, 45.20% Fe, 58.4% Mn, 88.4% Pb, and 31.3% Zn.	[102]

According to **Table 5**, the most important and significant area within the biotechnological process of metals is focused on the microbial oxidation of sulfide minerals. The aqueous environments associated with mine discharges and mining sites are typically characterized by low pH, high concentrations of heavy metals, and, in some cases, elevated temperatures. Despite these conditions and environments, certain microorganisms not only survive but also thrive and reproduce. In these environments, microorganisms utilize reduced sulfur species and certain metals in solution as their primary energy source, resulting in the solubilization of valuable metals [13][17].

Fungal species such as *A*. *niger*, *P*. *simplicissimum*, and *P*. *purpurogenum* are among the most used species in bioleaching and offer advantages over bacterial bioleaching, including the ability to thrive at high pH values and a faster leaching rate [84]. In these studies, pH is a control variable that indirectly indicates the presence or absence of organic acid production during the fermentation processes. pH influences the growth and excretion of organic acids in filamentous fungi. When grown in an unbuffered medium, filamentous fungi often rapidly acidify their environment to very low, and sometimes detrimental, pH values [103][104].

The production of organic acids and other metabolites in the fermentation process is also influenced by the agitation rate. Agitation at low to intermediate levels, ranging from 100 to 300 rpm, increases with agitation speed, whereas agitation speeds between 500 and 800 rpm further enhance it. Citrate synthase activity decreases with increasing agitation speed, while aconitase and isocitrate dehydrogenase activities increase with agitation speed, favoring the transformation of citrate into oxoglutarate [75].

Amino acids such as glycine, histidine, and alanine have been used to test their effect on gold solutions, revealing that the initial dissolution of gold in histidine solution is faster than in glycine and alanine solutions. However, upon extended leaching, it was found that glycine dissolves gold more rapidly and to a greater extent than histidine and alanine [105].

Pulp density plays a crucial role in determining the feasibility of applying bioleaching on a commercial scale. Increasing the pulp density from 1% to 2% (*w*/*v*) leads to a significant reduction of 50% in both the volume of leaching media required and the size of the bioreactor. This reduction in size and resource consumption directly translates into a substantial decrease in bioleaching costs. In the bio-hydrometallurgical treatment of low-grade ores, it is common to utilize pulp densities of 10% or higher to maximize efficiency and productivity [106].

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