POSTĘPY MIKROBIOLOGII – ADVANCEMENTS OF MICROBIOLOGY
2022, 61, 4, 179–190
DOI: 10.2478/am-2022-019

MICROBIALLY-PRODUCED ORGANIC ACIDS AS LEACHING AGENTS FOR METAL RECOVERY PROCESSES

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Received in December 2021, accepted in July 2022

Abstract: Minerals have been important throughout history, but nowadays, their use has increased, as well as their extraction needs. Therefore, due to the growing demand for metals, and both the depletion of high-grade ores and their related environmental concerns, the mining industry has been forced to leave behind the past traditional techniques of metal recovery (use of inorganic acids), and adopt eco-friendlier alternatives, such as the utilization of weaker leaching agents, such as organic acids. Thus, the present review is focused on the use of microbially-produced organic acids as a promising alternative to conventional techniques in the mining industry, with emphasis on the following topics: a) the advantages and disadvantages of the use of organic acids for leaching purposes, b) the main microorganisms studied for the production of these organic acids, c) a summary of the latest reports on bioleaching as well as a comparison of the existent techniques; d) the explanation of leaching mechanisms where organic acids may be involved, to fulfill metal recovery; and, e) interactions between metallic ions and organic acids. The review of the current knowledge regarding the use of organic acids for leaching purposes seeks the visualization of relevant strategies that may be improved for metal-recovery processes, intending to develop circular economy practices that may have the potential to be implemented at an industrial scale.

1. Introduction. 2. Generalities of organic acids (OA). 2.1. Advantages and constraints of using organic acids (OA) for leaching purposes. 2.2. Obtention methods of organic acids. 3. Comparison between bioleaching techniques. 4. Recommendations to establish successful bioleaching process using microbial produced OA. 4.1. pH and temperature. 4.2. Pulp density. 4.3. Matrix. 5. Bioleaching mechanisms using organic acids. 5.1. Acidolysis and complexolysis. 5.2. Redoxolysis. 5.3. Interactions between organic acids (OA) and metals. 6. Summary

Keywords: bioleaching, biological synthesis, metal recovery, microbial processes, organic acids

1. Introduction

The use of minerals is of common relevance in daily life, which can go from eating foods rich in some specific elements or compounds to powering every single electronic device at home, considering in between a high number of applications [61]. Indeed, ancient civilizations realized the importance of minerals, giving birth to many mining techniques that have been modified, improved, and explored until nowadays; mining represents an important economic activity for many countries. In 2016, 903 billion United States Dollars (USD) were earned by the top 20 metal-producing countries, which are: China, Australia, United States, India, Russian Federation, South Africa, Indonesia, Brazil, Canada, Chile, Peru, Kazakhstan, Mexico, Germany, Poland, Turkey, Colombia, Congo Democratic Republic, Ukraine, and Ghana [25]. Being mining industry of enormous importance for socio-economical concerns, the processes for mineral extraction have put aside the environmental impact over the years, as most of the anthropogenic actions have done [80].

Both environmental and social impacts of mining activities may vary depending on the characteristics of the mining site and the type of ore therein [83], and such environmental consequences can be reflected at all the trophic levels, causing: a) loss of ecosystems, even preservation areas (fauna and flora); b) soil acidification, which ends up in the loss of agricultural fields; c) pollution problematics related to water and atmosphere, due to contamination by metals; and finally, d) health problems in humans [33, 64, 83].

Besides these environmental issues, mining is facing other challenges, like the depletion of high-grade mineral deposits [7, 98], which makes harder (or even useless) the metal extraction processes commonly employed. Thus, the future of the mining industry, as we know it, seems troublesome. Currently, it is vital to employ greener processes to help the achievement of results while diminishing environmental and health impacts [60, 67]. Therefore, sustainable actions in different fields, such as extraction processes, are evidently supported in various countries like Australia and Canada [53], where biomining is gaining force, being

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successfully used for the extraction of several metals (Co, Cu, Ni, and Zn). In this respect, it has been reported that the 20% of Cu world production comes from the heap or the stockpile bioleaching [31].

Additionally, the main way to obtain mineral resources over the years, until now, has been through mining extraction activities. However, such activities seem to be attached to a clock due to new regulations around the world, which are demanding to diminish environmental impacts; consequently, ways to obtain metals are no longer focused exclusively on mining, but also in their recoveries through other sources, like e-wastes [9, 26, 27, 37, 54, 57, 60] or industrial residues, such as spent catalysts [8, 20, 40, 50, 59, 71, 81]. Regarding traditional mining techniques, pyrometallurgy is mainly used in high-grade ores [14, 42], leaving aside the low-grade deposits due to cost issues. These latter ores represent a new challenge, inciting the appearance of novel processes, such as hydrometallurgy, which can be employed even if the mineral amounts are low [14]. Therefore, hydrometallurgy represents an opportunity not only for low-grade ores but also for recycling processes.

Leaching processes in extractive metallurgy have usually employed inorganic acids (IA) due to their relatively low costs [16, 52]; however, these are not the only leaching agents. Chelating agents like diethylenetriamine pentaacetate (DTPA), ethylendiamine tetraacetate (EDTA), and nitrilotriacetic acid (NTA) have shown good efficiencies. Regrettably, they are not considered biodegradable, due to the environmental effects they may cause, especially when there are leakages into the ecosystems [34, 47, 86]. If well, there are other alternatives like alkaline leaching [9, 39, 54], this technique needs additional leaching steps using other acidic lixiviants in order to extract metals like Cd and Cu, making the processes more complicated and expensive [47]. In the look of more sustainable options, there has been studied the use of organic acids (OA) for leaching purposes, like oxalic, citric, malic, and succinic acids, among others [60, 86], and are reported to be less toxic to many biological communities than IA, apparently, because of the complexing capability they present. This complexing characteristic allows the reduction of metal concentrations that may be considered toxic. Also, OA are much easier to dispose and are biologically degradable [10]. Therefore, this review is focused on the use of microbially-produced OA as a promising alternative to conventional techniques for metal extraction in the mining industry and the recovery of metals from industrial residues.

2. Generalities of organic acids (OA)

OA are low-molecular-weight carbon compounds capable to form complexes with various elements [10]. Their structure is composed of carboxylic groups (-COOH). They consist of aliphatic monobasic carboxylic acids, from formic acid up to the C18 acids [43]. It is known that they are thermally stable, leave no negative impacts on the environment, and usually form strong chelates [22]. It has been reported that there are two forms to classify OA, and this classification can be according to their molecular weight or the number of carboxylic groups. In the first case, they can be of low-molecular-weight OA (LMWOA), if they have five carbons or less, or high-molecular-weight OA (HMWOA) if they have more than five carbons [6]. Examples of LMWOA include acetic, fumaric, oxalic, citric, and tartaric acids; they are found in milimole concentrations in soil, and those amounts are higher in the rhizosphere than in bulk soil [86]. Regarding HMWOA, it is known that they are also present in the soil; however, their content is still undefined. Most HMWOA are referred to as humic and fulvic acids. Both LMWOA and HMWOA possess the capability to form complexes [15]. Therefore, OA have been widely used as additives in foods, and for metal detoxification, which refers to the ability to control the solubility of heavy metals by complex reactions or chelation [72].

2.1. Advantages and constraints of using organic acids (OA) for leaching purposes

The use of OA is versatile due to their characteristics. One of them is their ability to inhibit microbial growth [12]; OA like acetic, lactic, and propionic acids, and their mixtures, have shown bacteriostatic and bactericidal properties [79]. These properties have been exploited by the food industry, by incorporating them as food additives or preservatives. Nowadays, bactericidal activity has been implemented in polymeric films used as food packaging [12]. Besides their antimicrobial activity, some of the OA are also known for their chelating properties and their biodegradability. These characteristics boosted the implementation of them as leaching agents. Table I shows the main differences between OA and IA.

2.2. Obtention methods of organic acids

Naturally, LMWOA are released by root exudation, organic matter decomposition in soils, and the production of microbial metabolites. Oxidative stress, high levels of Pb and Fe, as well as low concentrations of Ca and P, promote higher rates of OA from roots [86]. OA can be also chemically synthesized by oxidation of alcohols, carboxylation of alkenes, or hydrolysis of esters [19]; however, their synthesis has not been suitable for large-scale production because the raw material needed for their obtention is expensive and yields are low. Hence, microbiological production becomes an important economic alternative for the chemical production of OA [10].

Table I
Comparison of the reported characteristics of organic and inorganic acids in leaching processes

Organic acids (OA)	Inorganic acids (IA)	References
Less emission of hazardous gases	High emission of sulfur, chloride, and nitrous oxides	[35]
Serve for soil nutrient acquisition, mineral weathering	Can lead to high consumption either of water or chemicals	[29]
Less risky manipulation during the process.	Risky manipulation during the process.	[82]
Biodegradable	Non-biodegradable	[20, 35]
Delay the corrosion of equipment	Cause prompt corrosion of equipment	[82]
Can be used more than once in metal recovery processes	Cannot be reused in metal recovery processes	[35]
Are costlier than IA, but the process is considered cost-effective due to the environmental impact	Have low cost, but the process is not considered cost-effective due to environmental impact	[37]
Solely act as leaching agents; hence, separation nd purification are still needed	Solely act as leaching agents; hence, separation and purification are still needed	[35]

2.2.1. Biological synthesis of organic acids

OA are building-block chemicals that can be produced by microbial processes, besides chemical synthesis. Biological synthesis of OA is possible because most of them are natural products of microorganisms or intermediates in major metabolic pathways [85]. OA are formed mostly through microbial fermentation, and to do so, either carbohydrates or related substrates are used; many anaerobic and facultative microorganisms can produce OA during fermentation processes [68]. In general, the biological production of OA for bioleaching purposes has been focused on citric, malic, oxalic, and gluconic acids.

Important contributions have been made on this subject by studying OA-producing microorganisms such as *Aspergillus* species [11, 28, 45, 66, 75, 89, 91]; *Penicillium* species [3, 22, 46, 73, 76, 94, 100]; fungal consortia [44, 62, 69, 77, 93]; and bacteria like *Enterobacter aerogenes* [30].

Although it is known that several microorganisms possess the ability to produce this kind of compounds, like the 64 strains of Ascomycota and Basidiomycota reported by Liaud et al., [56], authors like Deepatana & Valix [21] report that *Aspergillus* and *Penicillium* have been preferred as OA bio-fabrics, mainly because of their ability to produce high amounts of these metabolites [58], which makes them microorganisms of relevance for this purpose.

3. Comparison between bioleaching techniques

Bioleaching using OA is still considered a new subject. According to Clarivate Analytics, during the last 5 years the total amount of articles published, including early access articles related to this subject, were 18 (Fig. 1), and doing a broader search from 1980 to 2021, a total of 42 publications were found.

Bioleaching studies reported to date employed diverse techniques for the production of relevant metabolites related to these processes, including OA. These analyses, performed under different conditions, assessed how this metabolite production affects the recovery of metals, in both one-step [4, 5, 58, 65] and two-step [95] direct bioleaching processes (microorganisms and matrix together); and in indirect methodologies (produced metabolites and matrix) [4, 5, 58, 65].

Considering the reports found, it seems that two-step bioleaching (where the microorganism is incubated a few days before being in contact with the matrix) reduces the toxic effects produced by spore germination and fungal growth, and accelerates the bioleaching process in comparison to the one-step methodology (where both microorganism and matrix are incubated at the same time) [95]. Additionally, it has been stated that an increasing pulp density, with both one-step and two-step techniques, results in a decrease of efficiency, which can be attributed to growth inhibition by metal toxicity, affecting metabolite production [74]. Finally, spent-medium techniques (indirect

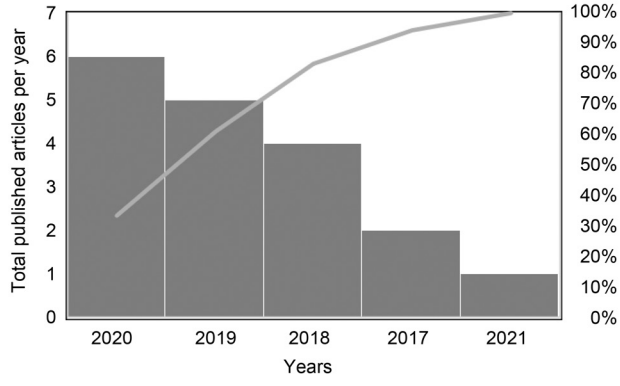


Fig. 1. Published articles from 2017 to 2021 related to bioleaching with OA

Data was taken from Clarivate Analytics in 2021; keywords used for this search were organic acids, bioleaching, metal recovery, and fungi.

Table II
Bioleaching at laboratory scale for metal recovery from industrial wastes using OA-producing microorganisms

Microorganisms	Leaching agent (mg/L)	Temperature (°C)	Time (days)	RPM	Pulp density % (w/v)	Recovery (%)	References
Mixed fungal cultures: *Purpureocillium lilacinum* (71.9%) and *Aspergillus niger* (27.9%) were dominant species. Others (0.2%) include: *Pseudallescheria* sp., *Malassezia obtuse*, *Tomentella* sp., *Davidiellaceae* sp., *Talaromyces* sp., *Fungi* sp., *Herpotrichiellaceae* sp., *Meyerozyma guilliermondii Wickerhamomyces anomalus*, and *Malassezia furfur.*	Oxalic 1022.4 Citric 5533.2 30 Gluconic 894.6	30	27	300	8	56.1 Cu 15.7 Al 20.5 Pb 49.5 Zn 8.1 Sn	[93]
Aspergillus niger	Citric 8131, 8064 Oxalic 1095, 973 Malic 1212, 1086 Gluconic 2065, 2153	Room temperature	21	120	0.092	98.57 Zn 43.95 Ni 64.03 Cu	[94]
Aspergillus niger	Less than 14000 of gluconic acid, less than 4000 of citric and oxalic acid, less than 3000 of malic acid	30	30	130	1	100 Li 94 Cu 72 Mn 62 Al 45 Ni 38 Co	[11]
Penicillium simplicissimum	Citric 5237 Gluconic 3666 Oxalic 1287 Malic 188	30	15	130	1	100 V 40 Ni	[76]
Kombucha-consortium (the bacterium *Komagataeibacter hansenii*, and the yeast *Zygosaccharomyces lentus*)	Gluconic 25500 Acetic 9608	Room temperature	14	300	2.8	(stationary bioleaching) 5.2 of REE* (shaken-mode bioleaching) 7.9 of REE	[44]
Aspergillus niger	Oxalic 17185 Gluconic 4539 Citric 1042 Malic 502	60	7	130	9	83 V 30 Ni	[75]
Aspergillus niger	Gluconic 2126 Malic 1251 Oxalic 1170 Citric 8078	30	30	130	2	69.8 Al 60.0 Ti 25.4 Fe	[89]

*REE, Rare Earth Elements.

biolixiviation) are limited by the content of metabolites produced in relation to pulp density; therefore, optimization of metabolite production is a key factor for increasing efficiencies [17].

More specific results from the last 5 years of direct and indirect bioleaching with OA, at a laboratory scale (mainly fungi), are shown below. Studies about industrial wastes (Table II), ores (Table III), and catalysts (Table IV) were included in these results; considering all of them, the following points can be observed: a) most of the work related to metal recovery has been performed regarding residues, rather than ores; b) concentrations of the OA obtained from the microorganisms (mainly fungi) were low, mostly milimole, comparing with concentrations normally used in leaching with commercial reagents; c) depending on the matrix composition, the percentage of elements recovered varied; however, matrices with Cu, Zn, Li, Ni, and V content reached recovering percentages from 50–100% (w/v) of each element. Overall, it can be concluded from these studies that, besides getting low OA concentrations, positive results can be achieved when using OA for bioleaching purposes, making it a promising technology, especially for recycling processes.

Table III
Bioleaching at laboratory scale for metal recovery from ores using OA-producing microorganisms

Microorganisms	Leaching agent (mM)	Temperature (°C)	Time (days)	RPM	Pulp density (% w/v)	Recovery (%)	References
Enterobacter Aerogenes	Mixture of malic, gluconic and acetic acids < 18 for both direct and indirect bioleaching	30	18	120	1	(direct bioleaching) 2.55 Ce 0.57 La 0.36 Nd	[30]
					2	(indirect bioleaching) 0.66 Ce 0.16 La 0.12 Nd	
Aspergillus sp.	Non-characterized supernatant	37	20	150	2	79 Mn	[65]

Table IV
Bioleaching at laboratory scale for metal recovery from catalysts using OA-producing microorganisms

Microorganisms	Leaching agent (mM)	Temperature (°C)	Time (days)	RPM	Pulp density (% w/v)	Recovery (%)	References
Gluconobacter oxydans	Gluconic < 30	30	1	150	1.5	RPP* maximum 2% of REE**	[77]
						FCC*** catalyst 49% of total REE	
Alternaria alternata	Not reported	30	2	150	1	8285.3 mg/kg V 6662.0 mg/kg Al 4973.8 mg/kg Si 3990.2 mg/kg Mo 177.7 mg/kg Mg 118.2 mg/kg Fe	[81]
					5	29.9 mg/kg As 9872.7 mg/kg Al 6839.0 mg/kg Si 2115.8 mg/kg Mo 1903.0 mg/kg V 279.6 mg/kg Mg	
Aspergillus niger	Citric and Gluconic < 98	30	60	130	1	3% La	[66]
					3	52% La	
					5	33% La	

* RPP, Retorted phosphor powder; ** REE, Rare earth elements; *** FCC, Spent fluid catalytic cracking

4. Recommendations to establish successful bioleaching process using microbial produced OA

Bioleaching processes involving OA can be done using either bacteria or fungi; however, as mentioned before, most of the studies to date are focused on *A. niger* or *Penicillium* spp. [21], mainly because of the following advantages that fungi present: a) fungi like *A. niger* can grow under alkaline pH, so alkaline residues can be treated; b) fungi-leaching processes are considered to be faster than bacterial ones due to the shorter lag phase presented by fungi; and, c) most fungi have the ability to excrete lixiviants, like OA, through Krebs Cycle. Nonetheless, fungal leaching is costlier than bacterial leaching [92].

Concerning OA bioleaching there can be found studies focused either on exploring the ability of some microorganisms for metal recovery (mainly fungi) through different bioleaching techniques or optimizing metal recovery processes. Regarding optimization, it can be done by finding the right parameters to operate the bioleaching processes, like temperature, agitation, pulp density, among others, or even by using genetically modified microorganisms. From the authors that have explored optimization, Amiri et al. [4] achieved the recovery of 99.5% Mo, 45.8% Ni, and 13.9% Al; Biswas

& Bhattacharjee [17] obtained 70.49% Ni and 66.93% Co, while Mafi Gholami et al. [58] reported the recovery of 71% Co, 69% Mo, and 46% Ni. Unfortunately, the results obtained in many bioleaching studies are hard to compare, due to the differences in the techniques employed (direct or indirect bioleaching); the diversity in the evaluation of the parameters, like matrices (ore, industrial residues, etc.) used; and growth conditions for the microorganisms; which all may influence metabolite production. In this regard, Amiri et al. [4] and Amiri et al. [5] stated that the ability of some microorganisms to produce OA as metabolites is not enough to use them for bioleaching purposes, because it is necessary to consider that their metabolite production will be influenced by the pH, the temperature of incubation, the balance amounts of C, PO_4^{3-}, and N (which are essential compounds of the medium), the pre-culture period, the concentration of the inoculum used, the pulp density, the bioleaching period, etc., besides the metallic charge of the matrix and the intrinsic metal resistance of the microorganisms used (in case of direct bioleaching) [96]; each one of these points will be explained below in a deeper way.

Medrano et al. [36] mentioned that to establish a successful bioleaching process, it is basic to understand the specific characteristics of the pre-culture medium, inoculum, growth of the microorganism used, and its resistance to metal ions; specifically, this latter property will allow deciding whether direct or indirect bioleaching is the most appropriate. For example, some pre-culture conditions may help to increase the efficiency of the process due to the cell density, so metabolite production may begin before being in contact with the matrix. This is profitable for the microorganism, as it could result in a decrease of the toxicity caused by the metal charge [96].

4.1. pH and temperature

The pH of the medium will provide conditions for the mechanisms of acidolysis (acid) and complexolysis (alkaline). As to temperature, evaluated by Musariri [67], and Zhou [99], it can be observed that specifically for indirect bioleaching or leaching (no microorganism involved), an increase in temperature helps to improve metal recovery and may diminish the time of the processes. For direct bioleaching, the temperature must be inside the optimum range for microbial growth [36].

4.2. Pulp density

The use of high pulp densities is feasible for indirect bioleaching, also known as spent media, where the matrix is in the presence of the metabolites without the microorganism. If bioleaching is direct, the metallic charge in the system may lead to toxicity that affects culture growth and, hence, metabolite production may be inhibited [96], as has been mentioned before. Authors like Ning et al. [55] and Li et al. [70] evaluated the effect of pulp densities for spent Li-ion batteries, while Zhou et al. [99] used light-emitting diodes (LEDs) for the same purpose. All of them reported that high pulp densities affected metal-recovery efficiencies. Additionally, they stated that low pulp densities reduce the contact area between the matrix and the lixiviant, facilitating bonds between them [99].

4.3. Matrix

The bioleaching process will always be influenced by the matrix. The content of the matrix can be in insoluble phases, and minerals could be completely encased, causing incomplete digestion [48]. Rene et al. [78] mentioned that, for bioleaching purposes, it is necessary that the bonds between metal ions and ligands are stronger than the bonds between metal ions and solid particles. Besides, the particle size of the material is also important, as Mazurek et al. [59] found that reductions of the particle size, ~ 180–250 μm, increased V recovery, and sizes under that range did not significantly affect V leaching but produced better results for K and Fe. Moreover, Gu et al. [41] reported that large surface-to-volume ratios accelerated the reaction rate, where 45 μm was found as the optimum particle size to improve metal recovery.

5. Bioleaching mechanisms using organic acids

Several authors, like Ilyas et al. [49], Mishra et al. [63], Rene et al. [78], Srichandan et al. [87], Vakilchap et al. [89], and Wu & Ting [92] reported the existence of four different mechanisms during bioleaching processes, which help to solubilize metals: acidolysis, complexolysis, redoxolysis, and bioaccumulation [49, 63, 78, 87, 89, 92]. Qu et al. [74], Qu & Lian [73], and Rasoulnia et al. [76] indicated that acidolysis is the most important and main mechanism for bioleaching [73, 74, 76]. Rasoulnia et al. [76] highlighted that the OA produced by microorganisms are part of both complexolysis and redoxolysis mechanisms, while the amino acids present in the spent medium will perform complexolysis [76]. Regarding metal bioaccumulation in fungi, it is known that the mycelium takes an important part in it, by acting as a sink for the metal ions present in the medium.

5.1. Acidolysis and complexolysis

The OA produced by fungi are metabolites of relevant interest for diverse processes in the food industry, cosmetic industry as well as recovery of metals. When

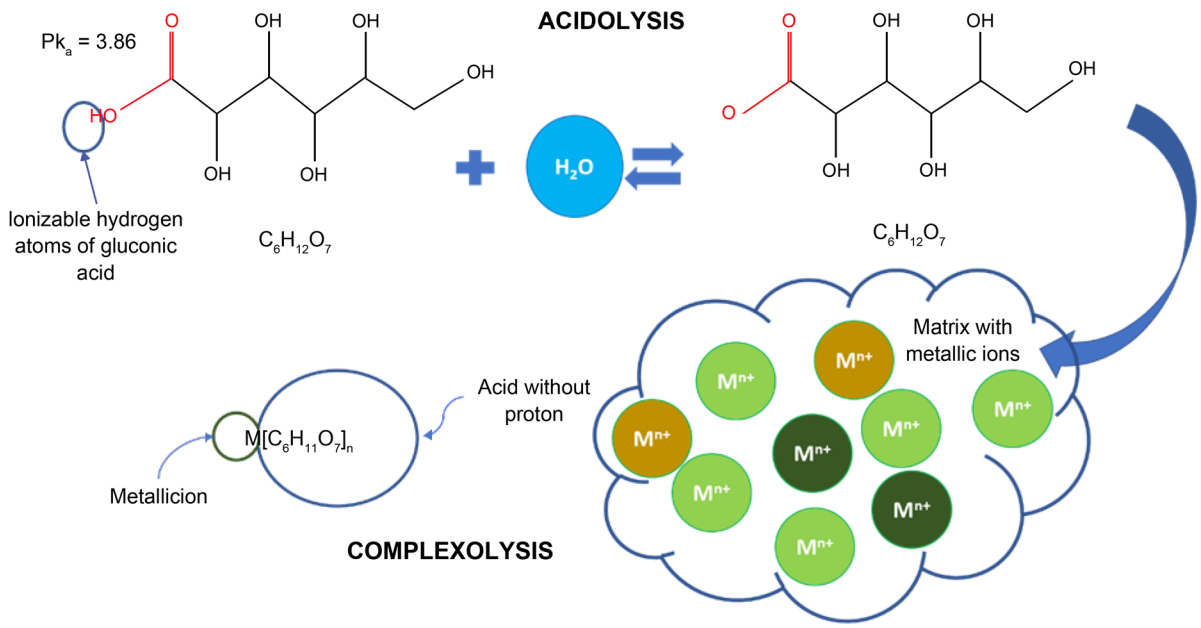


Fig. 2. Acidolysis and complexolysis mechanisms during metal extraction processes

these microorganisms excrete OA in metal-recovery processes, the hydrogen ions of the OA start to decrease the pH (acidolysis), occurring later the formation of metal complexes (complexolysis), until the OA are consumed, causing then a pH increment [11]. Therefore, protons participate in acidolysis while anions in complexolysis [66, 89], allowing to get almost a complete dissociation of the OA. Consequently, it can be presumed that if one mole of OA dissociates, like of gluconic, oxalic, or citric acids, there will be produced 1, 2, and 3 moles of protons, respectively [4]. Rasoulnia & Mousavi [75] complemented this information by emphasizing that, during all the direct bioleaching processes, the number of protons will vary depending on the ability of each microorganism to produce metabolites under specific stress conditions.

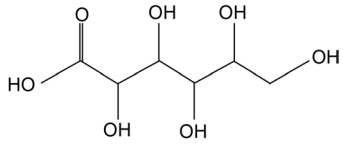
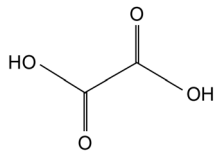
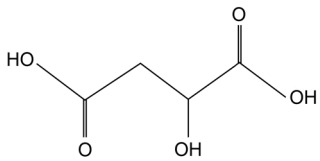
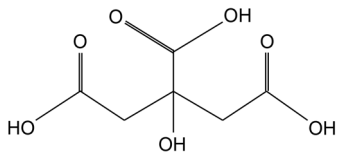
It has also been mentioned that acidolysis and complexolysis may be considered as the foremost mechanisms involved in fungal leaching processes, especially with solid wastes, being both processes highly dependent on the pH value of the system [75]. Regarding the reaction speed of both mechanisms, Rasoulnia et al. [76] reported that acidolysis is faster than complexolysis. Moreover, there has been stated that metal ions solubilized during acidolysis will be stabilized in complexolysis [11]. Figure 2 illustrates both acidolysis and complexolysis mechanisms.

As it can be observed, the acidolysis mechanism acts by liberating protons to the medium, around the surface of the metallic compound, once they are in contact with water. Later, metals are separated from the surface of the compound [7, 74]. Rene et al. [78] explained that protons excreted during acidolysis weak the metal-ion bonds, causing the metal to go into solution, and that to guarantee successful leaching, it is necessary that the bonds metal ions-OA are stronger than those of metal ions and solid particles from the matrix, to achieve either bioleaching or leaching processes [78].

Regarding complexolysis mechanism or ligand-induced metal solubilization, Amiri et al. [4] mentioned that it comprises the solubilization of metal ions, due to the complexing capabilities of molecules, by complex formation or chelates [45]. Complexation depends on the concentration of metals and anions in the solution, as well as the pH and the stability constants of complexes [11]. OA are bound to complexolysis mechanism by their carboxylic groups; thus, chelating agents can form soluble complexes with certain metallic ions such as Cu, Fe, Pb, Mn, and Ca [32]. Horeh et al. [45] gave examples of some OA complexes, including oxalic acid with Al, Fe, and Mg; citric acid with Mg and Ca, and tartaric acid with Fe, Ca, Si, Mg, and Al.

Chelate formation occurs due to an equilibrium reaction that can proceed in forward and backward directions; besides, it will depend on both the dissociation constants (acid strength in solution) and the stability constants (the relation between the chelated metallic ion and the free metallic ion), which will change along with pH variations in the medium. Regarding pH, it is known that chelates can lose stability in mediums with low pH (2–3) or high pH (10–12) [2]. Stability constants play a key role to understand the chelation order in complex matrixes, where the first chelate to be formed will only be the one with the highest tability constant; thus, the highest stability constant will always displace the lowest. Moreover, if there exists an excess of a chelated agent, other chelates with different elements can be formed, too. Otherwise, the

Table V
Reactions involved in acidolysis and complexolysis mechanisms for metal recovery

Organic acid	Acidolysis reactions	pK_a	Complexolysis reactions
Gluconic 	$C_6H_{12}O_7 \rightarrow C_6H_{11}O^-_7 + H^+$	3.86	$n[C_6H_{11}O^-_7] + M^{n+} \rightarrow M[C_6H_{11}O_7]_n$
Oxalic 	a) $C_2H_2O_4 \rightarrow C_2HO^-_4 + H^+$ b) $C_2HO^-_4 \rightarrow C_2O_4^{2-} + H^+$	1.25 4.14	a) $n[C_2HO_4^-] + M^{n+} \rightarrow M[C_2HO_4]_n$ b) $n[C_2O_4^{2-}] + M^{n+} \rightarrow M_2[C_2O_4]_n$
Malic 	a) $C_4H_6O_5 \rightarrow C_4H_5O_5^- + H^+$ b) $C_4H_5O_5^- \rightarrow C_4H_4O_5^{2-} + H^+$	3.40 5.11	a) $n[C_4H_5O_5^-] + M^{n+} \rightarrow M[C_4H_5O_5]_n$ b) $n[C_4H_5O_5^{2-}] + M^{n+} \rightarrow M_2[C_4H_4O_5]_n$
Citric 	a) $C_6H_8O_7 \rightarrow C_6H_7O_7^- + H^+$ b) $C_6H_7O_7^- \rightarrow C_6H_6O_7^{2-} + H^+$ c) $C_6H_6O_7^{2-} \rightarrow C_6H_5O_7^{3-} + H^+$	3.09 4.75 6.40	a) $n[C_6H_7O_7^-] + M^{n+} \rightarrow M[C_6H_7O_7]_n$ b) $n[C_6H_6O_7^{2-}] + M^{n+} \rightarrow M_2[C_6H_6O_7]_n$ c) $n[C_6H_5O_7^{3-}] + M^{n+} \rightarrow M_3[C_6H_5O_7]_n$

metallic ion-chelate agent with the highest stability constant will precipitate, while the other metallic ion-chelate agent will dissolve [90]. Besides, some metals are more sensitive to the formation of chelates than others, which is relevant for metal recovery. A preference to form chelates has been observed on elements that have a biogeochemical meaning, like Fe, Co, Mn, Cu, and Zn [84]. In addition, Rasoulnia et al. [76] recommend that, for the complexolysis to occur, the metal ion needs to be previously solubilized (acidolysis mechanism) [75].

Below (Table V) are shown the reactions of the most studied OA (gluconic, oxalic, malic, and citric acids) in bioleaching processes, including both acidolysis (liberation of protons and pKa values) and complexolysis (OA^- metallic complex formation) mechanisms, previously reported, where Mn^+ and M represent the metal ions [28, 74].

5.2. Redoxolysis

In redoxolysis, metals are mobilized from the matrix through oxidation and reduction reactions [11], by generating a direct electron transfer from metallic ions to microorganisms through the oxidation of Fe^{2+} to Fe^{3+}. This process depends directly on the redox potential present in the medium [24]. In microorganisms, part of this mechanism acts by shifting the oxidation-reduction potential of the growth medium [23]. The reduction of metal ions occurs in acidic environments [7]. As to metal mobility, this will augment according to the metallic ion and its oxidation state [87].

As it can be inferred from the information above, many possible bioleaching mechanisms may work simultaneously during direct bioleaching, and this fact is in agreement with the information presented by Bahaloo-Horeh et al. [11], who mentioned that the three mechanisms: acidolysis, complexolysis, and redoxolysis can occur concurrently. In the case of indirect bioleaching, which only involves metabolite production, it does not entail bioaccumulation due to biomass, because it is not present during the process.

5.3. Interactions between organic acids (OA) and metals

Most of the explanations given by researchers about OA and metals rely on the function of a broad range of mechanisms, and they also point out the variability of the extraction efficiencies, like in the case of Geng et al. [38], who found that high amounts of OA influence the diversity and concentrations of metals that can be recovered. However, little is known about the specific behaviors of OA with specific metal ions. The difficulty to understand these behaviors can be caused by the inherent complexity of the processes, which depend on many factors, such as the antagonistic effects between elements, the chemical form of metals, the properties of the matrix where metals are embedded, the application of pretreatment methodologies [18], and the

leaching time (some OA require more time to dissociate hydrogen ions) [51].

In general, OA are known to get complexed with heavy metals, and their extraction ability is related to the number of hydroxyl and carboxyl groups, as it is known that OA with two or three carboxylic groups can form chelates with structures of 5 or 6 rings [38]. Ji et al. [51] emphasized that, theoretically, OA would be expected to have better results than IA, due to both their acidity and complexing abilities; besides, these characteristics could affect the saturation of leaching solutions or could change the speciation of metal ions, meaning that metals could become less toxic. However, OA are still weak acids and, in practice, their efficiencies are lower than the ones obtained with IA.

Regarding matrix behaviors, Banerjee et al. [13] mentioned that, in matrices such as coal ashes, elements such as Al, Si, Fe, Ca, and Mg are present in the form of aluminosilicates, and the recovery of the metals contained therein is strongly related to the type of leaching agent used; that is, the leaching behaviors of IA and OA are different. In the first scenario, IA either destroy or dissolve mineral phases almost completely, contrary to OA, which can barely break them. Therefore, mineral phases are rarely leached in the latter case, and greater selectivity is achieved with the use of OA.

Citric and malic acids have been reported to promote high leaching efficiencies, especially for the mobilization of Cu, which can be attributed to the complex formation [38, 88, 97]. Additionally, positive results have been also obtained with Cd, Cu, and Pb using citric and malic acids [1], where Cu was the metal most highly recovered, being this recovery of around 36% with citric acid and 39% with malic acid; there was also achieved almost 65% of Cd recovery with oxalic acid.

Malic and citric acids achieved heavy Rare Earth Elements (REE) recoveries of around 30 to 37.5%. However, contrasting results have also been obtained in some cases, like the ones reported by Banerjee et al. (2021), who evaluated the leaching capabilities of five OA: tartaric, citric, lactic, malonic, and succinic acids (commercial reagents), for the recovery of REE, and for Al, Si, Fe, Na, Ca, and Mg, as well [13]. In this study, results showed that the highest leaching efficiency was found when tartaric acid was used, followed by the one obtained with lactic acid. As to the other OA evaluated (succinic and malonic acids), they achieved the lowest recoveries of REE. It was not expected that both tartaric and lactic acids could present better results than citric acid, because citric acid has usually been reported with the best metal-removal efficiencies, and the common way to explain the potential for metal removal of citric acid relays on the total number of carboxylic groups present in the structure of this organic acid (three carboxylic groups). So, this has been one of the explanations given to understand why citric acid has got the highest efficiencies among other OA (with less than three carboxylic groups). Therefore, the results of the latter study described raised more questions and set the precedent that the use of OA for bioleaching processes still needs further study. Thus, under the right conditions, OA could be a potential alternative to IA use at an industrial scale for metal-recovery processes, either when they are used as individual leaching agents or as a complex mixture of various OA when they are biologically produced.

On the other hand, oxalic acid strongly acidifies the leaching medium; therefore, it can facilitate the mobilization of some metals, like Zn, through an acidolysis mechanism [28], or of other metals present in matrices as waste printed circuit boards (WPCB). Additionally, it is known that oxalic acid can help the formation of oxalates in most bio-leaching cases that involved a variety of metals in the matrix. In this regard, authors have reported the formation of oxalates with metals like Cd, Cu, and Pb from soil polluted with metals [1], Ni, and Cu from WPCB [28], and REE from calcination product of a coal coarse [51]. The study published by Ji et al. 2020 also evaluated the potential of some OA to leach REE, where malonic and oxalic acids were evaluated as lixiviants, among other OA; it was found that both OA produced low metal recoveries. Thus, it was suggested by the authors that the low recoveries obtained by malonic and oxalic acids could be due to similarities in their molecular structure; however, this was not studied in deeper detail [51].

As it was mentioned through this document, the mechanisms involved in the recovery of metals will vary depending, first, on the bio-leaching process, and second, on the lixiviant used. Mechanisms as acidolysis, complexolysis, and redoxolysis are expected to happen in both direct and indirect bioleaching with OA, where acidolysis will occur first, and then complexolysis. Regarding the lixiviant, results have shown that all OA will have a different impact on metal-recovery efficiencies and will show some preferences for certain metallic ions, like in the case of citric and malic acids, which appear to have a preference for Cu. However, further studies are necessary to understand in which cases (depending on the matrix and metallic content) a specific OA or a mixture of OA is more appropriate for metal recovery. This could improve efficiencies or even help with metal selectivity, and furthermore, the use of OA would be eco-friendlier.

6. Summary

To the knowledge of the authors, there are not currently available deeper studies that explain the synergistic reactions among microbially-produced OA. Therefore,

research about OA mixtures and how their proportions may influence metal-recovery, results is an area of opportunity. As to reaching high efficiencies that could compete with IA, the following steps are suggested: a) first, the selection of the microorganism to use is crucial, being the ideal microorganism the one that naturally possesses high yields of OA production; b) later, the microorganism could even be genetically modified, to boost OA production of interest; c) subsequently, investigations should focus on adequate growth media (less costly), that does not affect the yields of OA, to enhance the potential to be implemented at an industrial scale; d) finally, bioleaching conditions should be optimized.

Throughout this review, there has been established the potential of OA for metal-recovery processes, whether they are commercial reagents or microbially-produced OA, mainly because of their advantage, as being an eco-friendlier option, compared to IA. As to which type of OA is more appropriate to employ, the information compiled here indicates that the synergistic activity of various microbially-produced OA, even in milimole concentrations, is as effective or even may have a greater potential compared to a single OA (commercial reagent) in M concentrations, which makes them a promising alternative for bioleaching processes, that should be further studied and optimized.

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