Chapter

Biotransformation of Metal-Rich Effluents and Potential Recycle Applications

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Abstract

In this chapter, it was introduced about the metallurgic effluents, and their potential to be converted into some feasible coproducts for industries. Some possibilities to introduce circular economy in the context of metallurgic effluents, and in the same way, some techniques to promote bioremediation using microorganisms and products from them were also described. Reported studies, as well as some perspectives to use metal-rich effluents in agriculture and soil quality improvement, were also shown. Copper effluents were kept as the main candidate for sustainable use, as a potentially interesting material for circular economy approaches.

Keywords: copper, metals, nanotechnology, microorganisms, agriculture

1. Introduction

Since the Stone Age, minerals have played an important role in the development of civilization, with mining activity being present from the beginning to the present days of society [1]. In fact, humanity is currently consuming mineral resources at an unprecedented rate of 70 Gt/year, resulting in the highest per-capita levels of resource consumption in history [2]. The excessive use of mineral resources results in a substantial generation of different kinds of wastes including liquid effluents.

These are wastes discharged from industrial, commercial, or domestic facilities and usually may contain many types of pollutants, including chemicals, heavy metals, salts, and pathogens, which can have harmful effects on human, animal, and environmental health. Regarding its end destination, effluents can be sent to treatment plants located right near the source of the effluent, usually private facilities, or common treatment plants farther from the generation point.

Although many effluents can be fully treated, those containing metallics or persistent organic pollutants pose many challenges to the current remediation techniques. Due to the challenges faced in treating such waste and its high cytotoxicity, good practices in industry consist of an "*in situ*" treatment, avoiding its relocation and transportation [3].

As regards the treatment of metal-rich effluents, traditional physicochemical methods, such as chemical precipitation and adsorption reactions, have been applied for many years to remove heavy metals from wastewater. However, these methods could have some problematic limitations, including high costs, generation of great amounts of sludge, as well as low efficiency in the removal of contaminants [4, 5]. Therefore, it is important to separate and preferably, as mentioned, treat these metal effluents *in situ*, since traditional techniques are not suited for treating heavy metal-based liquid wastes. For example, the sludge that is generated in the common effluent treatment is poisoned by the metals and a prolonged exposure to this effluent may induce resistance in the microbiome of the treatment plant by metal absorption in the long run. The observation of these processes leads to a new field of remediation, the so-called bioremediation.

Bioremediation has emerged as a promising alternative for the treatment of metal-rich effluents due to its effectiveness, low cost, and eco-friendly nature [6]. Bioremediation could be defined as the use of living organisms, such as bacteria, fungi, algae, and plants, to remove or transform hazardous substances from the environment [6, 7]. Microorganisms have evolved various measures to face heavy-metal stress, via processes such as transport across the cell membrane, biosorption

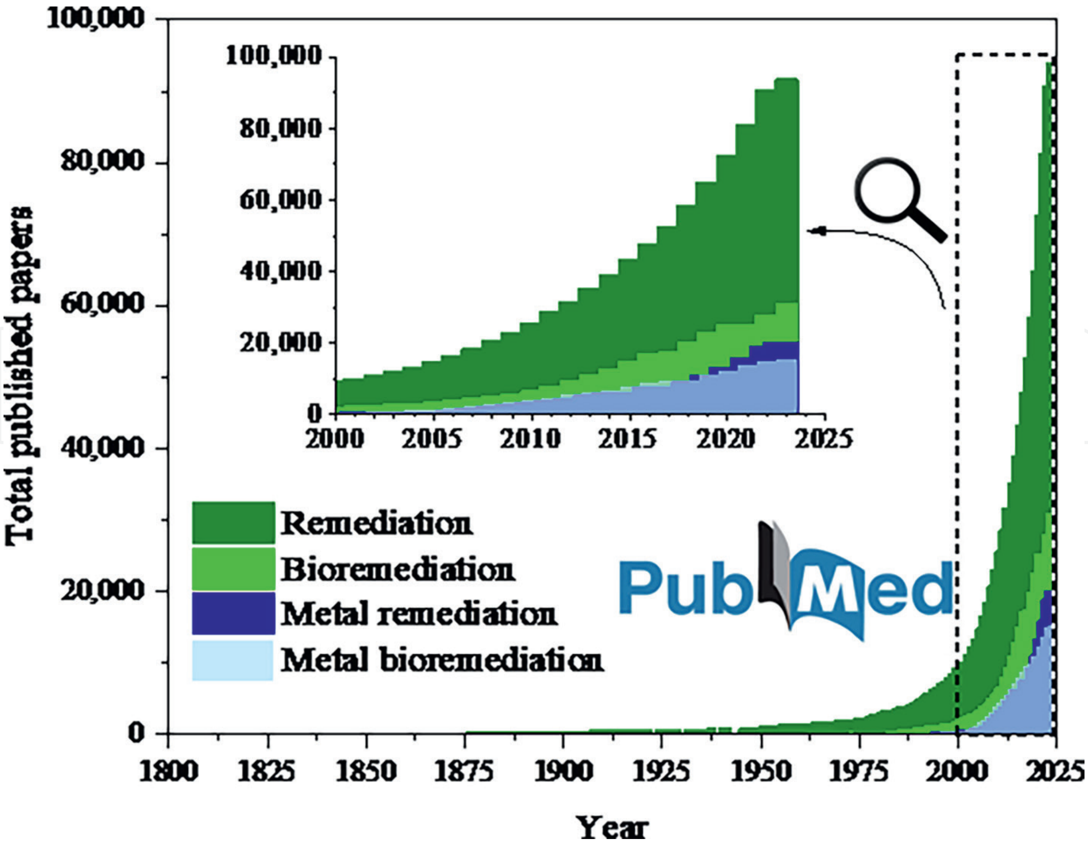

Figure 1.
Published papers registered in PubMed by year in the areas of remediation, bioremediation, metal remediation, and metal bioremediation. Data shown until April of 2023.

to cell walls, and entrapment in extracellular capsules, precipitation, complexation, and oxidation-reduction reactions [8]. Since many microorganisms already present mechanisms to intake and use metals in their metabolism as micronutrients, these organisms can be used to accumulate large amounts of heavy metals from the mining and metallurgical industries [9]. In nature, this intricate relationship is responsible for the metal biogeochemistry leading to the mobilization or immobilization of metal species [10]. First cited in 1969 [11], metal bioremediation has gained significant attention in the past 20 years, being responsible for approximately half of the total bioremediation papers published, as can be seen in **Figure 1**.

This chapter focuses on the score during 2003–2023 when the bioremediation evolved from theory to application. To showcase the fast-paced development of this technology, from 1969 to 2002, almost 800 papers were published, and in the past two decades however, more than 14,000 papers were published citing metal bioremediation. This shows the expansion of metal bioremediation and its relevance for metal industries' circular economy aiming at eco-friendly approaches in metal-rich effluents' treatment.

2. Early years (2003–2010)

As mentioned earlier, at the beginning of the twenty-first century, bioremediation processes were already known but faced practical limitations. Before this period, the relationships between many metal species and microorganisms have already been established, and microorganisms have been suggested for remediating metals from liquid wastes.

The bioremediation process can occur through different pathways, such as biosorption, bioaccumulation, biomineralization, and biodegradation. Biosorption involves the passive binding of heavy metals onto the surface of microbial cells that do not even need to be alive for this process to occur. Bioaccumulation involves the active uptake of heavy metals into the cells. Biomineralization involves the precipitation of heavy metals as insoluble compounds, while biodegradation is related to the breakdown of heavy-metal compounds into less toxic forms. The chosen approach may change considering the effluent metal concentration and type [4].

Some of the most common metals found in effluents include arsenic, lead, cadmium, chromium, copper, nickel, silver, and zinc [12, 13]. These elements are present in a plethora of effluents originated from different types of industries. Some industries produce effluents with a prevalent metal, usually coming from its main substrate. For example, Pb is commonly used in batteries and ammunition; Cd is also commonly used in batteries and coatings, while Cu is normally used in electrical wiring and plumbing, as well as other applications. However, some industries can produce some effluents with a mix of metals as, for example, mining industries, electroplating facilities, and paint manufactures. This mixture of different metals usually shows a difficult situation for the bioremediation processes of these industrial effluents.

In fact, metal effluents can be produced at many concentration ranges, but the traditional methods fail to be economically viable at low concentrations that usually range from 1 to 100 mg/L [14], thus increasing costs of separation and processing. On the other hand, at low concentrations, bioremediation processes stand out since the microorganisms can easily adapt to the prevalent conditions if compared to traditional physicochemical methods.

The first form of bioremediation of metals can be passive biosorption using biomass. These first efforts were also interested in the recovery of the metal species since environmental regulations were starting to compel industries to shift to cleaner methods [15]. At this time, the high metal-binding capability of many biological materials had already been described in the previous decade (in the 1990s) including algae, bacteria, and fungi, many of them, isolated from food industries. Many of these biosorption processes did not require the use of whole cells of microorganisms, using the presence of metal-binding molecules into the biomass to capture the metals from the effluent. The described process could not be influenced by the metabolic cycle of the biomass and it is commonly referred to as "passive uptake." This uptake could be analyzed using biosorption isotherm curves, evaluating the influence of the sorption process conditions [8]. These studies were focused on synthetic effluents, treating them with prepared biomass material, often using chemicals to increase the absorption into the biomass. These reported biosorption studies of a single metal on dead biomass, for example, Ni sorption onto dead mass presented sorption of 0.3% in low concentration synthetic effluents [8].

Despite being a kickstart to the technology, this process did not deal well under mixed metal effluents, usually disrupting the process, which hampered industrial applications [8, 13]. In addition, the biomass needed to be treated with chemicals, such as sodium hydroxide, detergents, formaldehyde, dimethyl sulfoxide, etc. One solution for this problem was the selection of microbial strains isolated from contaminated sites. The idea was that these strains, probably, already presented the capability to metabolize metal and promote bioremediation at some level, showing some adaptability to a wide range of concentrations [16, 17]. When the pure biosorptive metal removal was not viable, a consortium of microorganisms could be used, combining biosorption with other techniques, including bioaccumulation and mineralization [8].

It was also in these early years (2003–2010) that researchers started to establish that living and growing cells could uptake (the so-called bioaccumulation) great amounts of metal ions in solution in an extension even greater than that of the described biomass [8, 18]. These studies showed the capability of the metal to be internalized via an active uptake during the organism growth, increasing the metal uptake by joining the passive biosorption that initially happened. These changes resulted in metal concentrations to be higher inside the living cells than the biosorbed ones, increasing the efficiency of the bioremediation process.

Only at the end of the decade, high removal efficiencies were observed during the bioremediation of mixed metal effluents, such as mining effluents with bioremediation processes reaching 91, 96, and 99% of removal for Fe, Cu, and Al, respectively [19]. And in electroplating solutions using yeast (*Saccharomyces cerevisiae*) reaching 92, 92, and 87% of removal for Cu, Cr(VI), and Ni [20]. Both studies used subproducts of the food industry applying a cheap biomass originated from the microbial growth in the production of cheese [19] and wine [20]. From these studies, fungal biomass gained an increasing interest for removing metals. Fungal biomass is a subproduct of many industrial processes and fermentations, presenting a wide variety of morphologies [9]. The abundance of fungal mass available and the fact that usually fungi are already adapted to lower pH's made them ideal candidates for bioremediation of metal-rich effluents. Other studies showed some strains of *Aspergillus niger* have higher Ni biosorption capacities, if compared to dead pretreated biomass [8]. Also, the same fungal strains of *A. niger* showed high resistance to lead (II), however chromium (VI) ions caused inhibition of the microorganism that thrived in the presence of copper and lead [9].

To overcome this drawback, researchers obtained new microbial consortia from distinct contaminated matrices. For example, Jiménes-Rodriques et al. [19] collected samples of biomass from the Río Tinto, a river in Spain that presents an unusual acidic pH and elevated concentrations of metals. The obtained microbial consortia from this river were then applied to treat mine drainage by simply regulating the pH in an anaerobic condition, leading to efficiencies in metal removal between 91 and 99%.

It is important to notice the influence of the pH in the process since the conducted experiments by MacHado et al. [20] showed that by adjusting the pH of the treatment, it was possible to, selectively, remove some ions. At very low pH (around 2.0), the yeast surfaces were surrounded by hydroniums, enhancing the interaction of the biomass with Cr (VI). This is a very interesting approach, since using different pH ranges, it was possible to remove chromium ions selectively, avoiding poisoning of the sludge. The efficiency of Cr(IV) removal achieved using heat-inactivated cells of a flocculent strain of *Saccharomyces cerevisiae* was between 90 and 99% [20].

Although present at this time, phytoremediation was considered in its early stages. This technology is based on the growth of plant-based organisms on contaminated sites in a way that the plant can accumulate high quantities of metals. However, the efficiency of waste remediation is intrinsically related to the plant growth rate and the total biomass, making the process slow. In this scenario, the use of fast-growing plants was necessary [15], being the biomass of algae considered as an innovative solution [14].

In his influential review, Kosolapov et al. [21] described the most promising processes involved in the bioremediation of metals in constructed wetlands, i.e., engineered systems designed to mimic the natural processes of a wetland environment for the treatment of wastewater. This review also brought about the possible interactions of the microorganisms and plants present at these wetlands (**Figure 2**).

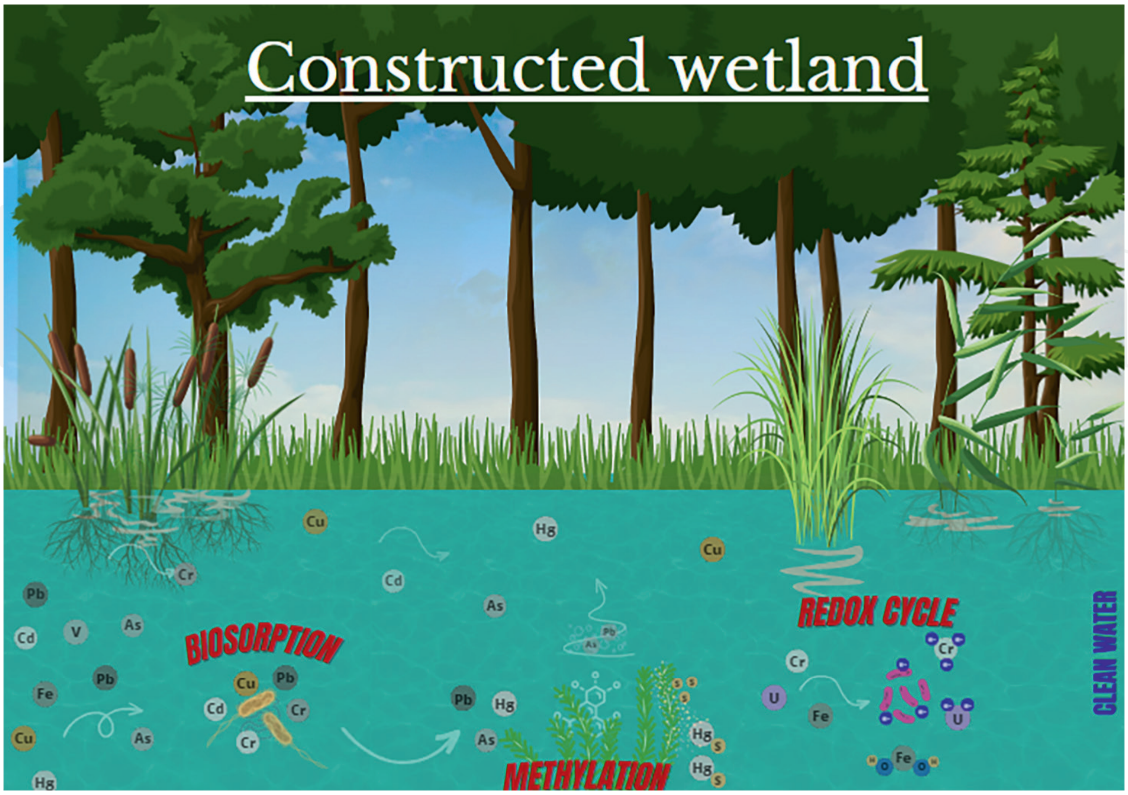

Figure 2.
Illustration based on the review from Kosolapov et al. [21].

These early years of metal bioremediation were summarized by Stasinakis and Thomaidis [22]. This study visited the reports of the biotransformation potential of many metals and metalloids, in experiments involving both, pure and mixed microbial cultures. Marked by great advances in the use of microorganisms in metal remediation, these early years cemented the fundamentals and experimental parameters needed for the implementation of an efficient bioremediation process to real effluents. However, despite the great advance in removal efficiency and elemental speciation, data on the biotransformation in Wastewater Treatment Processes were not enough. Fortunately, it did not take long before these data were enough for the bioremediation process to reach the next level of excellence.

3. Last decade (2010–2020)

This decade was marked by the application of bioremediation processes with high removal rates in real effluents and advances in isolating new microorganisms as alternatives to treat multimetal effluents [23]. For example, in 2013, a strain of *Acinetobacter* sp. was isolated from an effluent treatment plant in New Delhi, India, which showed high tolerance to the Cr (VI), exhibiting a high removal rate of Cr and Ni from a real effluent in an electroplating facility [23]. These chromium-resistant microorganisms used various detoxification strategies to counteract the Cr (VI), including enzymes'/metabolites' biotransformation from Cr (VI) to Cr (III), which is less toxic [24]. It is interesting to note that these resistant strains arise from the failure in treating metal-rich effluents, which indicated high content of these toxic metals in the environment. In another relevant work, Zhao et al. [25] isolated strains of *Sporosarcina saromensis* from offshore sediments in China, capable of tolerating super high Cr (VI) concentrations (~500 mg/l). This strain could remove 50–200 mg of Cr (VI)/L in just 24 h. This finding just demonstrated that with the rise in offshore pollution, tolerant strains have been commonly isolated from offshore and intertidal zones. From this study, more than 50 strains with the ability to tolerate Cr (VI) were isolated [25]. These findings confirmed that the current waste treatment was not adequate and that the environmental contamination by metals became a serious threat [26].

Cr-resistant *Bacillus* sp. was isolated from the effluent from a local tannery in Kanpur, UP, India [27]. Also isolated from the common effluent treatment plant of tannery industries, *Cellulosimicrobium* sp. was collected in Kanpur, India [28]. *Trichoderma viride* was isolated from electroplating industrial sludge [29]. Other examples are listed by Tarekegn et al. [26] and Kapahi and Sachdeva [30]. As well summarized by Tarekegn et al. [26] at the end of the decade: "Autochthonous (indigenous) microorganisms present in polluted environments hold the key to solving most of the challenges associated with biodegradation and bioremediation of polluting substances."

Although not many studies were carried out, it is also important to highlight the use of microbial mixtures. In 2015, Kang et al. [31] isolated four bacterial strains from an abandoned mine in South Korea. These bacteria lived in the soil of the mine and presented excellent Pb bioremediation capabilities. In 2016, Kang et al. [32] mixed the isolated microorganisms in different proportions and their results showed that when compared with a single strain, the mixtures presented higher growth rate, urease activity, and resistance to metals. These factors allowed the mixtures to exhibit considerably higher bioremediation capabilities when compared to single strains.

It was also in this decade that researchers started to better establish the role of microorganisms in the metabolisms of plants. For example, it was found that many endophytic organisms permitted the absorption of metal species [33]. This idea associated with the fact that many biomes were already being exposed to metals raises attention to phytoremediation. The term phytoremediation describes the utilization of plants and their accompanying microorganisms to remediate specific contaminants from soil, sludge, sediments, wastewater, and groundwater, either partially or entirely [34]. The ability of plants and associated microorganisms to accumulate essential metals in their metabolism enables them to accumulate other nonessential metals. It is suitable when the pollutants cover a wide area and when they are within the root zone of the plant [35]. The discovery of hyperaccumulators (plant species that naturally present a very high metal absorption) rekindled the interest in the area [34]. These plants can also be used with plant-growth-promoting bacteria, and these bacteria can improve the metal uptake by turning the metal species in the soil/effluent bioavailable to the plant [36].

Plant-like organisms such as algae also became a very interesting approach. Used mainly as biomass at the beginning of bioremediation, in this decade, the use of living algae marked an emerging trend of phytoremediation. Microalgae possess remarkable biological traits, including high photosynthetic efficiency and a simple structure, enabling them to thrive in challenging environmental conditions, such as the presence of metals [37]. In comparison with the traditional use of plants in phytoremediation, the use of algae presented lower toxicity constraint, high growth rate, and the formation of value-added products such as biofuels and fertilizer [37], bioremediating the metals and promoting carbon capture and circular economics. This new technique would gain even more attention in the next years, due to varied tolerance and specific responses as well as high metal bioaccumulation. Further advances in genetic engineering, metal immobilization techniques, algae pretreatment strategies, and integration with other emerging technologies are needed to fully unlock the potential of phytoremediation [37].

4. Recent years (2020–2023)

In recent years, the isolation of microorganisms continues to take place [38–40] and the intervening new technologies in genetic engineering [41] and omics sciences [42] are making new processes to remediate effluents the most viable solutions. Phytoremediation continued to grow and show many interesting results for metal bioremediation and even dye remediation [4]. Therefore, with the exponential growth of bioremediation studies (see **Figure 1**) using the most diverse kinds of microorganisms and approach based on real-life (multimetal) effluents, biotransformation of metal-rich wastewater is now initiating a new moment in which large-scale processes are close to reaching industrial application. Besides that, even the material produced by the bioremediation can be further utilized, as demonstrated by Amim et al. that showed the importance of the products generated by the biomass from wastewater treatment [43]. In addition, another disadvantage of bioremediation is attributed to its relative slowness when compared to physicochemical methods [44]. However, it is a green approach that presents higher capability and a lower cost that makes bioremediation the best choice aiming at sustainable development following circular economics rules.

Additionally, new approaches based on the union between traditional physicochemical methods and biological processes have been developed. Bio-electro-Fenton is a good example of such type of innovation. In this process, both organic molecules and metal ions are remediated by the microorganisms, while the traditional electro-Fenton process breaks down the persistent organic pollutants (POPs) into intermediates that can be metabolized. At the same time, when the degradation of pollutants to innocuous substances is carried out both by the traditional and biological processes, there is a synergy that reduces the costs of process operation. This is recent in the literature but results already indicate its great capacity for practical application, increasing the efficiency of the process and reducing the electro-intensive costs of the traditional electro-Fenton process [45, 46]. This is an important advance since persistent organic pollutants are an emerging problem in recent decades due to the increased consumption of medications and antibiotics and the fact that they are not 100 percent metabolized, increased fractions of these pollutants end up in the conventional sewage network [47, 48]. These substances present low biodegradability and high risk for human toxicity being generated during industrial production processes, especially those of chemical and pharmaceutical input production.

To degrade POPs, aggressive physicochemical methods are required due to the recalcitrant nature of these pollutants. The so-called advanced oxidative processes can oxidize most classes of recalcitrant pollutants. The Fenton process is an example of this class of treatment and consists in the production of hydroxyl radicals, highly oxidizing species (Eo = 2.80 V), capable of degrading practically any organic substance [49, 50]. This process is very old, being described in 1894 [51], and presents the aforementioned drawbacks, high cost, high sludge generation, etc.

By means of electrocatalysis [52] and photocatalysis [53], both electro-Fenton and photo-Fenton processes were proposed to decrease the Iron II addition by regenerating it through electricity or photon incidence. These processes, once the cutting edge of physicochemical processes, are being now united with biological remediation process to simultaneously treat persistent pollutants and present low cost and impact.

Bio-photo-Fenton [54] and bio-electro-Fenton [46] emerged as new frontiers and Colombo et al. [55] showed the reduction of pollutants in landfill leachate by combining photo-Fenton and biological processes. Silva et al. [56] observed an improvement in the biodegradability of leachate from an aerated lagoon using photo-Fenton powered by solar energy combined with a biologically activated sludge process. And Sirtori et al. [57] treated a real pharmaceutical wastewater by a solar photo-Fenton/biotreatment.

5. After treatment: reusing bioremediated metals in circular economy

Despite the low cost and high efficiency of remediation metals from effluents and soils, the biomass left still concentrates these metal species. Yes, the metal species are less toxic due to the bioremediation process, but at the current metal effluent generation rate, new solutions to further processes involving these metals are needed. The bioremediation process, as discussed, works very well in concentrations too low for traditional chemicals, allowing a low-cost and high-volume metal removal. After the remediation process, however, the metal is highly concentrated in the biomass making the chemical process to transform the metal viable. Therefore, in some cases, bioremediation serves as a pre-concentration step.

However, it is important to note that depending on the bioremediation process used, the metal may be accumulated in different ways inside the biomass. In the biosorption method, the metal can be simply desorbed from the biomass by changing the pH or the temperature of the biomass, or just by washing it with pure water [3]. In the case of bioremediation using growing cells, the metal can be fixed by different metabolic pathways of the bioremediation organism. As an example, the metal can be sequestrated in cell organelles, chelated, or even form ionic bond with the cell membrane [37]. Although some metals present preferential uptakes, this pathway can change from microorganisms to microorganisms, even more so in resistant microorganisms that develop specialty routes to intake metal ions [40]. An example can be *Pseudomonas* sp., depending on its strain, it can bioremediate Ni by accumulating in cytoplasm or in their extracellular polymeric substance [8]. This can be further complicated in consortia when different species concentrate metals by different pathways for the same metal [8, 30].

When simple leaching is possible, the acidic leaching solution removes the biosorbed metal from the adsorbent, leading to a concentrated metal solution that can be recovered by traditional methods such as chelation, reduction, or electrolysis. Moreover, it is also possible to integrate an acidophilic bioleaching with subsequent precipitation of the metals as insoluble sulfides by sulfate-reducing bacteria [8]. In the case of biomasses that are more difficult to leach the metals, usually the lysis of the cells is required. In this case, this can be promoted purely by acid leaching or heat treatment, upcycling the final biomass. A recent advance is the possibility of using simple heating or hydrothermal treatment to produce metal nanoparticles from metal released from the biomass, as demonstrated by Goswami et al. [58]. Other recent advances are related to the use of such metallic nanoparticles in agribusiness, as explored below.

5.1 Metallic nanoparticle development from biomass

With the increase in bottom-up nanoparticle synthesis, metal-rich biomasses are ideal candidates for the green generation of metallic nanoparticles. This type of nanoparticle production is based on the reduction of metal ions to produce metallic or metal oxide nanoparticles. In this context, Cu, Zn, and Ni, and noble metals, such as Ag and Au, present a very interesting opportunity, as bioremediation of these metals is already very well established with high recovery rates, and their nanoparticles are also a very well-established high-technology product [59–61].

This approach, called biogenic synthesis, is an economical and environmentally friendly alternative to chemical and physical approaches for the nanoparticle production [62]. Therefore, biogenic nanoparticles are a growing research field showing promising abilities of microorganisms to produce molecules, by the reduction of metal ions [63]. This can lead to a synergetic relation between the bioremediation process and the production of high-value nanomaterials [58]. In addition, metallic nanoparticles can also be capable of remediating effluents due to their unique properties of high surface-to-volume ratio, large surface area, and enhanced reactivity, which make them highly efficient in capturing and removing metal ions from wastewater [63–65]. Although both biogenic nanoparticles and bioremediation are growing fields, an end-to-end study of removing and recycling metals from effluent are not yet described in consulted literature.

Various types of nanoparticles have been explored for metal effluent remediation, including metallic particles such as iron, copper, nickel, zinc, and their oxides, as well as silica and carbon-based nanoparticles [66]. These nanoparticles can be engineered to have specific surface properties and functionalized with various coatings or ligands to enhance their metal adsorption capacity and selectivity [64]. The mechanism of metal removal using nanoparticles involves several processes, including adsorption, precipitation, ion exchange, and redox reactions. The nanoparticles can adsorb metal ions onto their surfaces, forming complexes through chemical interactions. They can also promote precipitation of other metal ions as metal hydroxides or other insoluble forms.

One advantage of nanoparticle-based remediation is that it can be applied to a wide range of metals, including heavy metals like lead, cadmium, mercury, chromium, and arsenic. Additionally, nanoparticles can be easily synthesized and functionalized, allowing for customization of their properties based on the specific metallic contaminants and wastewater conditions.

5.2 Agribusiness applications

As mentioned, the use of bioremediated metals in the production of nanoparticles can produce high-value products from the remediation processes. One interesting application of these particles is in the agribusiness. Agrochemicals play a crucial role in modern agriculture by providing tools for efficient and sustainable food production. Agrochemicals encompass a wide range of substances, including fertilizers, pesticides, herbicides, and plant growth regulators [67].

It is important to note that while these substances offer significant benefits in terms of crop productivity and protection, their use should be done judiciously and in accordance with recommended practices and regulations, since their indiscriminate use can lead to ecosystem degradation [68]. Appropriated application techniques, dosage, timing, and safety precautions are essential to minimize potential environmental and human health risks associated with agrochemical use. Weeds and insects are significant biotic factors that negatively impact agriculture by diminishing crop yield, production, and efficiency. Consequently, the widespread use of herbicides and insecticides is employed to mitigate these issues and achieve increased production by controlling or reducing pest populations [68]. In this scenario, agricultural nanoadditives have emerged in recent years [69]. These nanoadditives use the principle of high ratio between surface area and volume of nanostructured materials to potentialize microbicidal activity against pathogens, as well as to function as a nutrient, supplementing plant growth, being that these particles are more easily absorbed by the plant organism [70, 71].

Among the various types of metallic nanoparticles, silver-, copper-, and zinc-based particles are preferentially used as antimicrobial agents. Of these, silver is the [72] one that presents the highest cost in precursor materials and in their preparation. Meanwhile, both particles based on copper and zinc are simpler and cheaper to prepare and are already widely applied in tests with plant organisms [73]. In addition, copper is an essential micronutrient in many organisms, being an integral part of many proteins and metalloenzymes, playing a significant role in plant health and nutrition [73]. Due to the differentiated properties of materials at the nanometer scale, copper nanoparticles (Cu NPs) present greater absorption and efficiency than when compared to their other forms already used in the market [70, 73].

Similar to copper, zinc is also a critical micronutrient in both animals and plants, and it is necessary for the structure and function of a wide range of macromolecules, including hundreds of enzymes. Zinc is the only metal to be involved in all six classes of enzymes: oxide-reductases, transferases, hydrolases, lyases, isomerases, and ligases. Zinc ions exist primarily as complexes with proteins and nucleic acids and participate in all aspects of intermediate metabolism. In addition, zinc is one of the most rapidly depleted elements of soils [74].

One of the concerns related to the utilization of nanoadditives revolves around the environmental impact caused by the production process of these materials [72, 75–77]. Chemical routes are still the most prevalent in the literature for larger-scale productions, and only in recent years green routes are being prospected [78–83]. It is also worth mentioning that part of these green routes uses relatively noble parts of plants, such as starch, tea leaves, among others, using food supplies to produce particles [81, 82].

Recently, it has been reported in the literature the possibility of applying bioprocesses for the manufacture of these materials [84–88]. Bioprocesses are highly viable since they demand low costs for industrial utilities and can present high transformation power through the correct selection of transforming organisms [85]. In addition, these organisms allow the use of inputs of low added value as their metabolites, being several organisms specialized in their biome of origin in the degradation of low-quality residues, such as lignocellulolytic residues.

Still, in the literature, studies highlight the importance of bioprocesses in the production of biogenic nanoparticles, which have greater interactions with organisms [84]. This fact comes from the natural coating performed during its synthesis, and the particle is covered with several biomolecules contained in the reaction medium. In addition, biogenic nanoparticles are produced without the generation of coproducts, as in many cases from chemical routes.

However, it is necessary to emphasize that given their direct and intentional application in the environment, nano-agrochemicals can be considered particularly critical in terms of possible environmental impact, as they represent the only diffuse and intentional source of nanoparticles in the environment [89]. Precisely because they are involved in several biological processes, the metals have the ability to activate cell death pathways when in high concentrations [90–92]. It is worth mentioning that these nanomaterials also have the capacity for human toxicity and ecotoxicity, if at high concentrations. Therefore, there is growing concern regarding the indiscriminate use of nanoparticles, as often classical risk assessment tools can fail due to the lack of information about the life cycle of these materials [89]. In addition, the accumulation of nanoparticles in the soil results in their greater absorption through the roots of the plants, showing toxic effects and inhibiting the growth of the applied cultivars [72, 93].

To solve this problem, we can use substances that fix the nanoparticles, preventing their distribution in the soil of application. One of the most used scaffoldings for this purpose is activated carbon. This material has high surface area, low cost, and acidic sites. All these characteristics make this material widely suitable for the fixation of metal oxide particles, acting as a mechanism of slow and controlled release of the applied particles. This type of carbonaceous material can still be produced from several different sources of carbon, presenting already in the literature relevant results for several residual biomasses of processes. It is now referred to the activated carbon produced using biochar [94–97].

López-Vargas et al. [98] developed a study about the foliar application of copper nanoparticles (Cu NPs) in the production of tomatoes, using different concentrations, as a result, they obtained that the application of Cu NPs increased the firmness of the tomato fruits, consequently increasing the shelf life of the fruits, in addition to inducing the accumulation of bioactive compounds such as vitamin *C, lycopene*, total phenols, and flavonoids in tomato fruits.

Other studies in the literature showed benefits with the use of copper nanoparticles, such as the increase in photosynthesis and stomatal conductance in the cultivation of peppers (*Capsicum annuum*) [99], and in the case of exposure to copper oxide nanoparticles (CuO NPs), an increase in the nutrient quality in chive (*Allium fistulosum*) cultivation [100] and increased chlorophyll photosynthesis and antioxidant enzyme activity in mustard (*Brassica juncea*) [101]. Nowadays, the application of microbial seed coating processes for seed inoculation is also proposed, and studies show promising results [102–107].

In the light of all the discussed topics in this chapter, an interesting prospect of circular economic has arrived. By bioremediating metal-rich effluents, a metal containing biomass is generated [8]. The metal can then be extracted and transformed into nanoparticles [58], and the remaining biomass can be turned into biochar [95]. By impregnating the biochar with metal, this composite material can then be used as a plant growth promoter and bacterial inoculation support to use in the phytoremediation of metal-contaminated soils [97, 108].

6. Conclusions

Bioremediation is a broad and very promising approach regarding metal effluents. This chapter focused in to report information generated between the years 2003 and 2023, bringing some robust and applicable technological solutions for not only removing metals, but also looking to turn them into a valuable coproduct for new commercial segments to industries. Many techniques for metal bioremediation, applying microorganisms and/or their byproducts, were brought together. Overall, copper effluents could emerge as a promising candidate coproduct for environmental and sustainable reuse, applying circular economy approaches.

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