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RECOVERY OF METALS USING BIOMETALLURGY

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Abstract

Bacteria can live in extreme environmental conditions. They can bring about a wide variety of metal transformations such as sorption, reduction, oxidation, methylation and sulphidation. Bacteria interact not only with well-known metals such as iron, copper, silver and gold, but also with a wide range of rare earth metals. This paper reveals the current importance of biometallurgy worldwide and suggests new approaches and potentials by which this domain of technological development can contribute to a more sustainable bio-economy.

Bacteria-metal interactions

Bacteria can be classified as small prokaryotic organisms, typically of the order of a few micrometers in length. These organisms can be found all over the world, in soils, hot springs and wastewaters, as well as in organic matter and animals and plants. Therefore, their presence is highly important for the nutrient cycles of carbon, nitrogen, phosphorous and sulphur. Some specialised bacteria can live in extreme environmental conditions and are able to withstand either very high or low ranges of temperature, pressure, pH or heavy metal concentrations. Depending on the characteristics of the specific bacterial strain and its environment or application, bacteria can be found as pure cultures either as a collaborative consortium.

Through evolution, micro-organisms have learnt to interact with metals through a wide variety of mechanisms, like reduction, oxidation, methylation, sulphidation and sorption… Especially for the latter mechanism, bacteria have several particular characteristics to be an interesting sorbent material for metals in solution. Due to their small size and different structures on their surface, they can achieve very high specific surface areas (> 100 m^2/g living biomass). This high specific surface can provide a large number of sorption sites for metallic ions. Moreover, they have several free functional groups on their surface. Negatively charged carboxyl groups and positively charged amine groups have previously been shown to be important for the sorption of metals[1]. The variety of functional groups can allow for a selective sorption of metals. Since these groups are naturally present on the surface of the bacterial cells, they do not require functionalisation. This is an important advantage compared to more conventional sorbents such as activated carbon, which require a sometimes complex functionalisation in order to contain the required functional groups for metal sorption. A third important aspect is the fact that bacteria can grow in more complex 3-dimensional structures such as biofilms and granules. In these structures, bacteria are indirectly attached to each other by means of gel-like molecules such as polysaccharides, alginates and other biopolymers. These biomolecules provide, because of the functional groups in their structure (especially carboxyl groups), more available sorption sites for metallic ions. Bacterial sorption of metals occurs within a timeframe of several minutes to hours, as was described for Au[2] and for Ce[3]. Despite continuing increases in published research on biosorption, there has been little or no application in an industrial context[4].

It is known that bacteria can alter the oxidation state of metals by reduction or oxidation. The reduction process has mainly been described for Ag, Au and Pd. It results in the formation of extracellular, intracellular or periplasmic zerovalent metal nanoparticles. These nanoparticles can then be further applied as a catalyst (in the case of Au and Pd) or a disinfectant (in the case of Ag). De Corte *et al*. described a slow reduction of $AuCl_4^-$ (after 24 hours) to Au(0) by *Shewanella oneidensis* after a relatively fast biosorption of ionic Au onto the cells (within 30 minutes)[2]. The sorption and reduction of Au is believed to be mainly abiotic. The reduction of Pd was demonstrated for several species, among which *Desulfovibrio desulfuricans*[5], *Shewanella oneidensis*[6] and *Cupriavidus metallidurans*[7] are the most important ones. Some studies state that bacterial enzymes, especially hydrogenases are

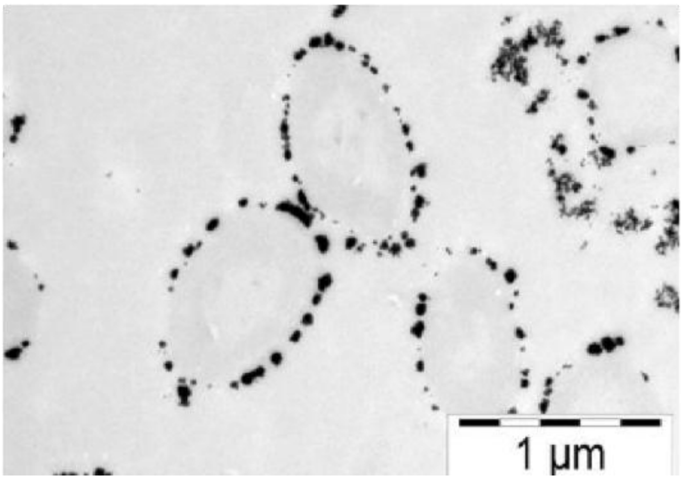

Figure 1: Transmission electron microscopy (TEM) image of palladium nanoparticles at the *Shewanella oneidensis* cell surface (after De Windt *et al*. 2005[6])

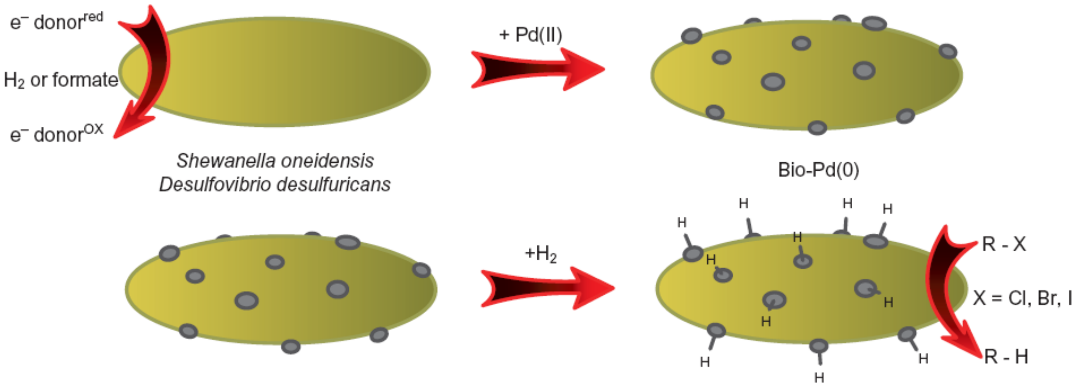

Figure 2: The application of bio-Pd as a catalyst: a two-step dehalogenation of halogenated substances with a bio-Pd catalyst and an external hydrogen donor (after De Corte *et al*. 2011[14])

indispensable for the reduction process[8], while other studies attribute the reduction to the presence of the electron donor following the sorption of the metal ions to the bacterial cell wall[9].

The resulting bacterial cells loaded with Pd nanoparticles, also referred to as 'bio-Pd', can further be applied as a catalyst, for example for dehalogenation of environmental contaminants[10] or for C-C coupling reactions in organic chemistry[11]. The organisms generally used for Pd reduction have already been used for the recovery of Pd from scrap leachates and metallurgical wastestreams[12]. The biogenic reduction of Pt using similar mechanisms as for Pd has also recently been described[13].

Other interactions are the methylation, the association with phosphates or the sulphide precipitation of metals. The latter process is based on the action of sulphate reducing bacteria. These bacteria reduce sulphate or elemental sulphur to sulphide in presence of an electron donor (*e.g.* H_2 or ethanol), resulting in the formation of insoluble metal sulphides. Currently, this process is being applied on an industrial scale to recover Zn and Cu from industrial effluents as ZnS and CuS.

Potential biometallurgical applications for recovery of critical metals

Biometallurgy is particularly suited for the recovery of metals from aqueous solutions or from low to medium concentrated solid materials. It can remove metals from diluted solutions and concentrate them to economically interesting concentrations.

Aqueous waste streams

For the treatment of aqueous waste streams, bacteria could be applied under different forms: as free suspended cells, in more complex structures such as granules and biofilms or strengthened by the addition of biopolymers like chitosan or alginate.

The main advantage of biometallurgical approaches is that these processes do not require solvents or aggressive and toxic chemicals. In contrast to electrometallurgical or pyrometallurgical processes, biological processes require relatively low amounts of energy. Energy is only required to maintain specific growth conditions for the bacteria or to intensify the contact between the bacteria and the waste stream. These low energy investments allow the possibility of treating waste streams with relatively low concentrations of critical metals, since treatment by more conventional and energy-intensive hydrometallurgical, pyrometallurgical or electrometallurgical techniques would result in a relatively low yield of critical material recovered per amount of energy invested.

In addition, bacteria can be considered as a renewable sorbent/reductant/producer of chemicals, since they can divide and grow continuously and relatively fast. The bacterial growth can be achieved in situ. However, the conditions of the waste streams to be treated will sometimes be unfavourable for bacterial growth. Bacteria can then be grown in a separate bioreactor with optimal growth conditions.

Table 1: Potentially interesting aqueous waste streams for biometallurgy containing critical metals at low concentrations

Aqueous stream	Critical metals present	Concentrations	Challenges
Hospital wastewater	Pt, Gd	µg/L	Extremely low concentrations
Wastewater from PGM[1] processing industry	PGMs[1]	Few mg/L	Aggressive streams, different metal speciations, interfering compounds
Washing liquid from used LCD[2] panels	In, Ga	µg-mg/L	Residues of Hg present
Others, to be identified	All	µg-mg/L	Characterisation of different streams urgently needed

[1] PGM: Platinum Group Metals, [2] LCD: Liquid crystal display.

Several types of aqueous waste streams could be targeted for applying biometallurgy; hospital wastewater and waste streams of industry (Table 1). Hospitals are producing wastewater containing Pt and Gd in very low concentrations (µg L^{-1} level). Because of the low metal content, these streams have a rather moderate economic value. However, an efficient treatment is required to limit the environmental impact. The neutral pH and presence of an organic carbon source (COD) makes these waste streams compatible with biology based systems.

Harder to treat are industrial waste streams, generated by industries that process platinum group metals (PGMs) or precious metals, such as industrial leachates containing a few hundreds of milligrams Pt or Pd per liter[7,15]. Despite of the low concentrations (mg L^{-1}), these streams, however, have a high economic importance due to the presence of highly valued metals (Table 2). The downside of this type of waste streams is the aggressive character of the wastewater.

Table 2: Platinum group metals (PGMs) and their current prices (January 2013)

PGM	Price (€/kg)
Platinum (Pt)	40 000
Palladium (Pd)	19 000
Rhodium (Rh)	30 000
Ruthenium (Ru)	3 000
Iridium (Ir)	26 000

After the application of biometallurgical techniques for the removal of the critical metals, there are different possibilities of downstream processing. When bacteria are applied as a sorbent of precious metals, these can, for metals such as Pd or Pt, be transformed relatively easily to zerovalent metal nanoparticles. The latter can in some cases be applied as a 'green' catalyst. The organic nature of the carrier material implies an application of the catalyst at relatively 'soft' conditions of pressure and temperature, for example in dehalogenation reactions under environmental conditions. If the application as a catalyst is not favourable, a type of sludge is created which can be processed by conventional hydrometallurgical, pyrometallurgical or electrometallurgical processes. The metals will be present at relatively high concentrations on an organic carrier. For instance, *Pseudomonas* species can reach 50 mg La sorbed per g dry matter[16] and by applying granular biomass metal concentrations up to 500 mg per g dry matter can be obtained[15], which can be incinerated or oxidised.

Solid waste streams

The most widely applied biometallurgical concept is the concept of ‘biomining’ or ‘bioleaching’[18-20]. It is based on the transformation of minerals through the microbial oxidation of iron and sulphur. It can be performed by a number of species, of which the mesophilic *Acidithiobacillus ferrooxidans* is the best known. By this process, Fe^{2+} and Cu^{2+} can be dissolved from the minerals pyrite (FeS_2) and chalcocite (Cu_2S). The overall reactions of both processes are:

$$FeS_2 + 14\ Fe^{3+} + 8\ H_2O \rightarrow 15\ Fe^{2+} + 2\ SO_4^{2-} + 16\ H^+$$

$$CuS + 8\ Fe^{3+} + 4\ H_2O \rightarrow Cu^{2+} + 8\ Fe^{2+} + SO_4^{2-} + 8\ H^+$$

Both processes are exergonic and permit microbial growth. Also Au can be extracted from ores by this process, since it is often included in the mineral structure of arsenopyrite. The technique of bioleaching is applied on an industrial scale to extract Fe and Cu from minerals where the metals are present as sulphide species. Most of these bioleaching installations are installed outside Europe. Large plants were installed in South Africa, Mexico and Chile. Ten years ago, Chile produced already over 4.6 million tonnes of copper per year in total. Bioleaching processes supplied about 10 percent of this amount. Actually, 25 to 30% of the world’s copper production is attributable to bioleaching[21]. In 2000, the annual world production of copper, cobalt, gold, nickel, uranium and zinc thus gained by bioleaching processes accumulated to about 3.6 million tonnes of metals, generating a surplus value of over 11 billion US dollars[22]. Nowadays, the number of large-scale bioleaching plants is still increasing.

Compared to chemical leaching, bioleaching has clear environmental advantages, is economically competitive and enables reductions in energy consumption as well as in pollution and waste generation. If acid leaching processes are considered within the biometallurgy context, these acids, mainly sulphuric acid, are produced from harmless sources of sulphur and are produced locally, in the proximity of the cells, resulting in an overall relatively low concentration.

The underlying mechanisms of bioleaching and microbial acid production could be applied for recovery of metals from different solid waste streams available in Europe. The lamp powder fraction, for example, of recycled End-of-Life fluorescent lamps and compact fluorescent lamps (energy saving lamps) are a rich source of rare earth elements (REEs), including the critical REEs europium, terbium and yttrium. From the phosphate fertiliser industry, the acidic by-product phosphogypsum can be used. These low concentrated solid waste residues typically contain several REEs, such as lanthanum, cerium, praeseodymium and neodymium. The application of bacteria and fungi for the mobilisation of metals from electrical and electronic waste materials is already investigated for some species. *Aspergillus niger* and *Penicillium simplicissimum* were both able to mobilise Al, Ni, Pb and Zn by more than 95% and *Thiobacillus thiooxidans* and *Thiobacillus ferrooxidans* could leach more than 90% of the available Cu, Zn, Ni and Al[22].

Process intensification

As bioleaching is a rather slow process proceeding normally at rates of 1 to 6 kg metal per m^3 reactor per day - for instance for bioleaching copper from flue dust[23,24] - process intensification technologies could be implemented. The use of ultrasound techniques can possibly stimulate bacterial growth and aid the leaching process[25]. Optimal ultrasound frequencies and conditions should be investigated. Moreover, ultrasound can also improve the process of bioleaching physically, by stimulating particle erosion and, by doing so, making the metals more available to the micro-organisms.

The process could probably also be intensified on a genetic level. Genetic parts of these organisms coding for the enzyme activities involved in bioleaching could for example be transferred to organisms which are easier to culture in fermenters and reactors. Hence, higher metal recovery rates could thus be obtained. Also introduction of genes involved in iron or sulphur oxidation in other organisms could be introduced in the bioleaching organisms in order to intensify the process. Genetic engineering could aim at increasing growth rates of organisms at the high temperatures and low pH which are required for the process. The possibilities of different molecular techniques for the purpose of improved bioleaching and biometallurgy should definitely be explored further.

Slag valorisation

Bottom ashes and slags of waste incineration processes can be seen as a third interesting solid waste stream, since metals as Al, Pb, Cr, Zn, Se, Sr, Ba and Cs are known to be present in µg - mg g^{-1} levels[26]. Heavy metals in bottom ashes may leach into soil and groundwater and pose long-term risks to the environment[27]. By applying bioleaching processes metals could be removed from these ashes and leaching to the environment could be prevented[19]. The metals are transferred from a solid to a liquid phase, where they can be treated by the hydrometallurgical or biometallurgical techniques described above. The biometallurgical potential for recovery of metals from bottom ashes is yet to be studied in detail. It is clear that biometallurgy again should aim at residues which are from an economic or energy perspective not interesting to treat chemically or thermally.

Conclusions

Bacteria can be used for the removal and recovery of critical metals from:

- Liquid waste streams through biosorption. The application of this technology is very interesting for diluted streams.
- Solid waste streams through the production of acids and bioleaching, possibly intensified by techniques such as ultrasound.

Bottom ashes and slags can definitely be a potential waste stream to recover metals biometallurgically. It is of utmost importance that the biological techniques are complementary with the more conventional techniques in order to obtain a maximum recovery with a minimum of environmental burdens and energy input.

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