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# BIOHYDROMETALLURGICAL METHODS FOR METALS RECOVERY FROM WASTE MATERIALS

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The article draws attention to recently conducted research of bacterial leaching of metals from various polymetallic waste. These wastes are the carriers of valuable metals: base metals, precious and platinum group metals (e.g. electronic waste, spent catalysts) or rare earth elements.

*Key words:* biohydrometallurgy, waste, raw materials, bioleaching,

## INTRODUCTION

Biohydrometallurgy, field of hydrometallurgical technology incorporating the use of microorganisms in the process of metals recovering from metal-bearing materials attracts a lot of interest of research teams. In biological processes, successfully used for the recovery of metals from low-grade ores or concentrates (e.g. copper bioleaching from chalcopyrites ores), scientists perceive the potential and point out an important role of microorganisms, they can play in the future during waste treatment processes. Therefore, next to the processes conducted on industrial scale for primary materials bioleaching, intensive research on the possibilities and efficiency of metals bioleaching from many types of waste are carried out (Figure 1). This interest results from the advantages attributed to biological methods. Biohydrometallurgical processing of solid waste is derived from natural biogeochemical metal cycles and reduces the demand of resources, such as ores, energy and landfill space. This technology is environmentally friendly(in comparison to chemical methods), is considered as a green technology (generates less amount of waste) [1-13] and can be an attractive alternative to currently used conventional recovery methods.

Although previous works were not processed beyond the stage of laboratory tests, these methods are considered to be promising ones, hoping they can lead to the development of more efficient and less costly processes. The activity of different groups of microorganisms, alkalophilic or acidophilic mainly mesophilic, moderate and extremely acidophilic bacteria are used in bioleaching. Among major groups of bacteria most commonly used are: acidophilic and chemolithotrophic

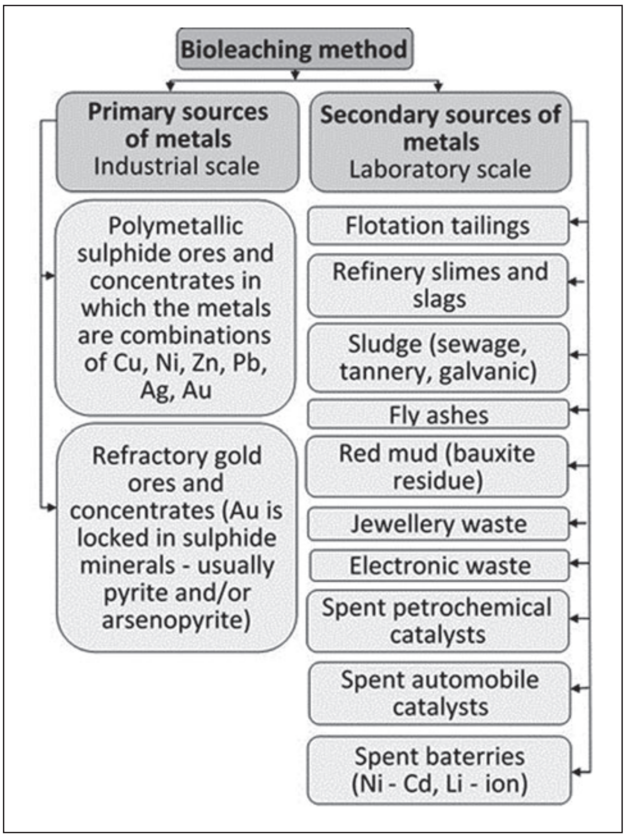


**Figure 1** Primary sources of metals and secondary waste subjected to bioleaching in industrial and laboratory scale

microbial consortia of: Acidithiobacillus ferrooxidans, Acidithiobacillus thiooxidans, Leptospirillum ferrooxidans and heterotrophs for example Sulfolobus sp.. In addition, microscopic fungi such as Penicillium sp. and Aspergillus niger are examples of some eukaryotic microorganisms used in bioleaching during metal recovery from industrial waste. Apart from the possibility of metals bioleaching in acidic environment in the biohydrometallurgical techniques, microorganisms able to form hydrocyanic acid (HCN) play an increasingly im-

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portant role resulting in biological process of leaching in an alkaline environment e.g. bacteria Chromobacterium violaceum, Pseudomonas fluorescens, Pseudomonas aeruginosa, or fungi - Marasmius oreades acidophilous [3].

There are many works regarding bioleaching methods of various types of waste containing valuable metals. These waste are often complex mixture of different materials and contain basic, precious metals as well as hazardous substances. Metals which were analyzed for their possible recovery can be divided into the following categories: (i) base metals (e.g. Cr, Pb, Zn, Cu, Ni), (ii) precious metals (Au, Ag and Platinum Group Metals - PGMs), (iii) special metals (Li, Rare Earth Elements - REEs), (iv) radionuclides (e.g. Th, U).

## BIOLEACHING OF BASE METALS FROM WASTE

Studies on extraction of base metals from waste were conducted with the participation of different microorganisms (Table 1).

These raw materials are characterized by material heterogeneity, containing various metals, their alloys asw well as plastics, glass and ceramics. An example of such complex matrix in terms of materials variety is electronic waste [3].

Table 1 **Examples of waste containing base metals subjected to bioleaching**

| Type of waste and extracted metals | Used microorganisms | Ref. |
|---|---|---|
| Fly ashes: Zn, Cd, Cu, Ni, Cr, Pb, Mn, Fe, Al | A. thiooxidans + A. ferrooxidans, A. niger | [1] [4] |
| Slag from copper smelter: Fe, Cu, Zn, Ni | A. ferrooxidans, A. thiooxidans Acidithiobacillus caldus, L. ferrooxidans, S. thermotolerans | [5] |
| Tannery sludge: Cr | A. thiooxidans | [6] |
| Sevage sludge: Cu, Ni, Zn, Cr | Iron oxidizing bacteria | [7] |
| Red mud: Pb, Zn, Cu, Ni, As, Ba, Cr, Fe, Zr | A. niger | [8] |
| Spent processing catalysts (oil refinery): Al, Co, Mo, Ni | A. ferrooxidans +A. thiooxidans | [9] |
| Spent refinery catalysts: Ni, V, Mo, Al | Iron/sulfur oxidizing bacteria A. niger | [10] [11] |
| Spent hydrocracking catalyst: Mo, Ni, Al | Acidianus brierleyi | [12] |
| Spent hydrocracking catalyst: Ni, Fe, W, Mo, Al | Penicillium simplicissimum | [13] |
| Electronic scrap: Cu, Sn, Ni, Pb, Zn, Al | A. ferrooxidans, A. thiooxidans, A. niger, P. simplicissimum | [14] |
| Electronic waste: Cu, Zn, Al, Ni | Thermosulfidooxidans sulfobacilllus + Thermoplasma acidophilum | [15] |
| Electronic waste: Cu, Pb, Zn | A. ferrooxidans, A. thiooxidans and mixture | [16] |
| Electronic waste: Cu | A. ferrooxidans, A. ferrooxidans +A. thiooxidans | [17] |
| Spent Ni - Cd batteries: Ni, Cd | A. ferrooxidans | [18] [19] |

One of the first studies on microbiological leaching of metals from electronic waste was carried out in presence of mixed bacteria of A. ferrooxidans and A. thiooxidans [14]. Authors observed toxic influence of waste on microorganisms. Bioleaching process was hindered and its dynamics was slowed down. It was believed that high Al concentrations (and the alkaline character of the non-metallic components) in the environment inhibited the growth of bacteria. Gradual adaptation of bacteria to the environment and the addition of acidifying agent improved the efficiency of the process. In such conditions Ni, Al, Zn and Cu were dissolved in solution with effectiveness close to 90 %. Since the publication of Brandl's work [14] much attention was given to the issue of metal bioleaching from electronic waste using A. ferrooxidans and A. thiooxidans or their mixture [2,15-21]. Results of these studies look promising. Metals (Cu, Zn, Sn, Ni, Pb and also Al) present in the waste were extracted (in many cases) at a high level of > 80 % and often even > 99 % efficiency.

A large group of waste rich in transition metals are catalysts used in the refining industry for the purification and upgrading of various petroleum streams and residues. Spent hydro-processing catalysts contain W, Mo, Ni, V, Co also Al and some organic contaminants (carbon and oils) [22]. Fungi of A. niger was used for leaching Ni, Mo, Al from spent refinery catalysts [23] and P. simplicissimum was applied for leaching W, Fe, Mo, Ni, Al from spent hydrocracking catalyst [13,22]. Adaptation of P. simplicissimum with different heavy metals present in a spent hydrocracking catalyst gave the extraction in the range 100 % of W, 100 % of Fe, 92 % of Mo, 66 % of Ni, and 25 % of Al with 3 % of pulp density (w/v). The main lixiviant in the bioleaching turned out to be gluconic acid. The production of primary metabolites such as citric, gluconic and oxalic acids play the major role in leaching metals from such wastes [23]. Some reports described bioleaching procedures applied to the recovery of metals by means of A. ferrooxidans and A. thiooxidans [9], iron/sulfur oxidizing bacteria [11] or thermophilic acidophilic archaea - Acidianus brierleyi [12].

The secondary batteries, including nickel–cadmium and nickel metal hydride batteries are used extensively in various areas as rechargeable energy supplier. Bioleaching tests to extract metals from spent Ni - Cd batteries were carrried out by using A. ferrooxidans [18,19] or using indigenous acidophilic thiobacilli in sewage sludge in continuous flow two-step leaching system [24,25]. Ni bioleaching efficiency was 45 % and 5,4 % for cathodic and anodic material respectively and Cd was leached in 100 % and 98 % for the same materials [18,19].

Red mud (bauxite residue) is the main polymetalic waste product of the alkaline extraction of alumina from bauxite by the Bayer process with high amounts of metals. Major elements in this waste are: Al, Fe, Si, Na, K, Ca Ti and also metals in lower concentration (e.g. As, Ba, Cr, Cu, Ni, Pb, Zn) [26,27]. Bioleaching of heavy metals from red mud was conducted by using A. niger [26]. During the bioleaching process, lasting 40 days, over 80 % of Pb and Zn, 67 % of Cu, 50 % of Ni, 44 % of As, 31 % of Ba, 26 % of Cr and about 11 % of Fe and Zr was leached, with optimum pulp density of 1 %. The leaching toxicity of red mud significantly decreased. The results showed that the main lixiviant excreted by the fungi was the citric acid. It was also indicated that the fungi had a favorable growth condition and organic acids production in the presence of 5 % (w/v) pulp density. Therefore, A. niger has a potential application for bioleaching of red mud.

## BIOLEACHING OF PRECIOUS AND PLATINUM GROUP METALS

Content of precious metals and PGMs in the waste determine the value of waste and profitability of its processing (electronic scrap or catalysts). Seemingly small concentration of these metals in electronic device unit (< 0,5 %) and catalyst (< 0,3 %) in terms of global sales is an important part in the production of precious metals [27,28] and their valuable source.

C. violaceum, P. fluorescens and P. plecoglossicida bacteria were used for extraction of gold, silver and platinum from electronic waste, jewellery waste and automotive catalytic converters, respectively [29]. These bacteria have an ability to produce hydrocyanic acid (HCN), which can dissolve gold. Bacteria demonstrated the ability to mobilize silver, platinum and gold in the form of cyanide complexes. Gold was extracted from shredded electronic scrap by both C. violeacum and P. fluorescens as dicyanoaurate $[Au(CN)_2]^-$, after 3 days. However C. violaceum proved to be more efficient regarding gold mobilization, reaching higher concentrations of dicyanoaurate. Only small amount approximately 0,2 %, of the total Pt present in the converter was mobilized. It is assumed that Pt mobilization is prevented by a passivating oxide film. However there is neither wider analysis nor an overall description of this phenomenon in literature.

Research on bioleaching of metals from electronic waste by using cyanogenic bacterial strains were also carried out by Kumar et al. [30]. Maximum metal mobilization exhibited single culture of C. violaceum and a mixture of C. violaceum and P. aeruginosa. C. violaceum was capable of leaching more than 79, 69, 46, 9 and 7 % of Cu, Au, Zn, Fe and Ag, respectively at an electronic waste concentration of 1 % w/v. Moreover, the mixture of C. violaceum and P. aeruginosa exhibited metals leaching of more than 83, 73, 49, 13 and 8 % of total Cu, Au, Zn, Fe, and Ag, respectively.

## BIOLEACHING OF SPECIAL METALS (Li, REEs) AND RADIONUCLIDES

Spent lithium-ion batteries are the main carrier and a source of lithium. The spent lithium ion batteries contain Li and also Co as an active cathodic material ($LiCoO_2$). Bioleaching of this cathodic material was carried out using chemolithotrophic and acidophilic bacteria A. ferrooxidans [31] or mixed culture of acidophilic sulfur-oxidizing and iron-oxidizing bacteria [32]. In these works not only the efficiency of the process has been studied, but the bioleaching mechanism has been interpreted as well. Depending on pulp density cobalt dissolution was about 56 – 65 % and lithium about 10 % [31].

Red mud (in addition to major elements and metals in lower concentrations) also contains rare elements (e.g. Sc, Y, La, Nd, Ga, Yt) and radionuclides (uranium and thorium) [25,27]. It was reported that significant ecological problems and considerable negative environmental effects were caused by radioactive elements and the alkaline content of red mud in various parts of the world [27]. Bioleaching of REEs and U, Th from red mud was conducted by using fungi isolated from red mud identified as Penicillium tricolor [26]. With increasing pulp density (2 %, 5 %, 10 %) there was a decrease in the leaching ratios of the REEs and radioactive elements. The maximum leaching ratios of the REEs and radioactive elements were achieved under one-step bioleaching process at 2 % of pulp density (incubating the fungi together with the red mud). Regardless of the leaching conditions and pulp densities, the leaching ratios generally increased with the atomic number of the REEs (except for yttrium and scandium). REEs (16 elements) were leached in the range from about 26 % to 80 % (depending on atomic number). The residual ratio of Th in the bioleached red mud after one step process at 2 % pulp density was approximately 55 %. It was also indicated that approximately 9.9 % of the Th was lost (i.e. neither in the red mud nor the leaching filtrate). Authors concluded that the bioaccumulation or biosorption of Th by used strain is responsible for the Th lost in the bioleaching process. These phenomena probably play an important role in removing the radioactivity.

## SUMMARY

A reflection of the great interest in using biological methods for the recovery of metals from waste can be the number of appearing studies. Biological leaching has been conducted in the presence of variety microorganisms and in a wide range of waste-carrying base, special and precious metals. In many cases promising results of metals extraction were obtained. Problems associated with metal toxicity towards microorganisms have been solved by their adaptation to high concentration of heavy metals. Although many problems associated with the selection of the optimum process parameters still remain to be resolved, increased efficiencies of bacterial leaching operations, make these processes more competitive in relation to conventional methods.

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