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POTENTIAL OF MICROBIAL FUNCTIONAL COMMUNITIES FOR HIGH-TECH CRITICAL METALS RECOVERY

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Abstract: According to European Commission reports published between 2010 - 2013, the development of European economy depends crucially on access to critical raw materials. Following the analysis performed by experts at European level, in 2011 was compiled and published a list of 14 critical raw materials, the so-called EU-14. In 2014 the list was updated with several new elements and one element (tantalum), was withdrawn from the list. The current list, being renamed EU-20, covers 20 critical raw materials including several high tech critical metals. Traditional mine exploitations are concentrated on using the deposits of ore extracted and processed by conventional techniques. The efficiency of metal recovery was variable over time and as a result, a significant amount of metal was discarded, most concentrations exceeding the current minimal permissible threshold. On the other hand, it is necessary the recovery of recyclable waste for reducing the risk of shortage of high tech critical metals. Therefore, it is necessary to develop new technologies for obtaining high tech critical metals, which is applicable to both primary and secondary sources of raw materials. Recovery of high-tech critical metals by processing ore, tailings or mine wastes, and recyclable materials can be successfully done with help of consortia or individual isolates of microorganisms, bacteria or fungi. Microorganisms interact with metals thus altering their physical and chemical condition. Isolation of individual strains and identification of microbial consortia that can be used in the design and development of effective biotechnological processes for the extraction of high tech critical metals is a current challenge of the scientific research in Europe.

Keywords: microbial communities, critical metals, high-tech industry, biorecovery, bioaccumulation

INTRODUCTION:

Raw materials and their applications are vital for the reindustrialization and competitiveness of Europe, in a world where a large proportion of primary resources are produced outside Europe and controlled by a small number of countries (with an important impact in their economies). In the past raw materials exploitation was focused in the economically high grade ore deposits, extracted and processed by conventional techniques. The metal recovery efficiency of these techniques was variable and not very high, and, as a consequence, is expected that a significant amount was discarded to the tailings dams.

According to European Commission reports published between 2010 - 2013, the development of European economy depends crucially on access to critical raw materials. Following the analysis performed by experts at European level, in 2011 was compiled and published a list of 14 critical raw materials - antimony, beryllium, cobalt, indium, fluorspar, gallium, germanium, magnesium, natural graphite, niobium, PGMs (Platinum Group Metals - platinum, palladium, iridium, rhodium, ruthenium and osmium), rare earths - yttrium, scandium, lanthanum and the so-called lanthanides (cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium), tantalum, and tungsten, the so-called EU-14 (* /* COM/2011/0025 final */). In 2014 the list was updated with six new materials – borates, chromium, coking coal, magnesite, phosphate rock, and silicon metal and one element (tantalum), was withdrawn from the list. The current list, being renamed EU-20, covers 20 critical raw materials including several high tech critical metals, Table 1, (** /* COM/2014/0297 final */). This list is going to be updated every three years.

Table 1. List of high-tech critical metals

Crt no	*Name of high-tech critical metals*	*Symbol*	*Observation*
1	Antimony	**Sb**	
2	Boron	**Bo**	metalloid
3	Beryllium	**Be**	
4	Chromium	**Cr**	
5	Cobalt	**Co**	
6	Gallium	**Ga**	
7	Germanium	**Ge**	
8	Indium	**In**	
9	Magnesium	**Mg**	

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Crt no	Name of high-tech critical metals	Symbol	Observation
10	Niobium	**Nb**	
11	Wolfram / Tungsten	**W**	
12	Silicon	**Si**	metalloid
13	Iridium	**Ir**	PGM
14	Osmium	**Os**	PGM
15	Palladium	**Pd**	PGM
16	Platinum	**Pt**	PGM
17	Rhodium	**Rh**	PGM
18	Ruthenium	**Ru**	PGM
19	Terbium	**Tb**	HREE
20	Dysprosium	**Dy**	HREE
21	Holmium	**Ho**	HREE
22	Erbium	**Er**	HREE
23	Thulium	**Tm**	HREE
24	Ytterbium	**Yb**	HREE
25	Lutetium	**Lu**	HREE
26	Yttrium	**Y**	HREE
27	Scandium	**Sc**	LREE
28	Lanthanum	**La**	LREE
29	Cerium	**Ce**	LREE
30	Praseodymium	**Pr**	LREE
31	Neodymium	**Nd**	LREE
32	Promethium	**Pm**	LREE
33	Samarium	**Sm**	LREE
34	Europium	**Eu**	LREE
35	Gadolinium	**Gd**	LREE

PGM - Platinum Group Metals; HREE - Heavy Rare Earth Elements; LREE - Light Rare Earth Elements;

Traditional mine exploitations are concentrated on using the deposits of ore extracted and processed by conventional techniques. The efficiency of metal recovery was variable over time and as a result, a significant amount of metal was discarded, most concentrations exceeding the current minimal permissible threshold. On the other hand, it is necessary the recovery of recyclable waste for reducing the risk of shortage of high tech critical metals. Therefore, it is necessary to develop new technologies for obtaining high tech critical metals, which is applicable to both primary and secondary sources of raw materials. Recovery of high-tech critical metals by processing ore, tailings or mine wastes, and recyclable materials can be successfully done with help of consortia or individual isolates of microorganisms, bacteria or fungi (Zhuang *et al*., 2015; Hennebel *et al*., 2015).

MICROBES AND BIOLEACHING:

The metals are involved in the development, metabolic activity and growth of bacteria, which are involved in turn in biogeochemical cycles of metals in nature. Metals can be toxic to microorganisms and interact because of natural geochemical events, can be generated by anthropogenic or by redistribution of metals in ecosystems. Sometimes, microbial activity can cause remobilization of metals from the waste water systems.

However, in spite of the metal toxicity there are many microbial species with the ability to grow in contaminated environments or has specificity to such an environment. It has been shown that organisms adapt to such an environment due to their ability to engage in metals speciation change, a phenomenon that increases or decreases their mobility.

Four main mechanisms are involved in the bioleaching process: acidolysis, complexolysis, redoxolysis and bioaccumulation. Leaching dead by chemolithotrophic and chemo-organotrophic leaching, the presence of siderophores, redox reactions, methylation and demethylation or biodegradation of organo-radionuclide complexes. Immobilization can occur by biosorption to cell walls, exopolymers, other structural components and derived/excreted products. Precipitation can be a result of metabolite release or reduction, transport, accumulation, intracellular deposition, localization and sequestration, and adsorption and entrapment of colloids and particulates (Gadd, 2010).

The biosurfactants synthesized by bacteria, fungi or yeasts are involved in bioaccumulation of metals. For example *Pseudomonas aeruginosa* can secrete rhamnolipid and *Candida sp*. Sophorolipid, important agents in bioremediation of soil rich in critical metals (Wang *et al*., 2009; Mao *et al*., 2015).

Gupta *et al*. (2015) stated that, statistically, from the bioprecursors, the biomass resulting from dead algae, fungi, bacteria, etc., recorded an average adsorption capacity of the metal ions by 110.86 mg / g, with a minimum of 14.7 mg / g and a maximum of 443 mg / g. This technique is used for the accumulation of metals in the aquatic environment. The advantages of this technique are the lack of metal toxicity influence on the organism involved, lack of nutrient needs, the ability of the biomass reusing.

The progress in electronics determined using the resources of rare earth metals, and most of them are not individual mined, but are found in the mines of the industrial metals, such as zinc, aluminum, copper and nickel. Because there are no known substitutes for some of these metals in their current functional uses, the recycling is going to be more important. (Ayres *et al*., 2013). Critical metals are used as electrical superconductors (She *et al.*, 2011), in the technology for producing the photovoltaic cells (Anctil *et al*., 2012).

Development of certain strains of *Methanocalculus taiwanensis* isolated from the Eril Shin estuary, Taiwan, is positively influenced by the presence of tungsten (Lai *et al*., 2002). Tungsten is the growing stimulator for *Methanococcus infernus*, also. This is a new species, with an optimum temperature of 85 ° C and methane-generating (Jeanthon *et al*., 1998). In 1999, Jeanthon *et al.* have found that a strain of *Methanococcus vulcanius*, able to reduce the elemental sulfur to hydrogen sulfide, it is enhanced the growth by the presence of tungsten, selenium and yeast extract. However, this is autotrophic bacteria and hyperthermophilic metanogenic. Tungsten, together with molybdenum causes phenotypic changes in the bacteria *Desulfovibrio vulgaris,* because they are involved in activation of some specific enzymes (da Silva *et al*., 2013). *Methyloversatilis discipulorum* is another species that shows a formaldehyde ferredoxin oxidoreductase with content of tungsten (Smalley et al., 2015). Feng *et al.*, 2016, were isolated from a mine tungsten a *Massilia putida* strain resistant to heavy metals and producing dimethyl disulfide.

Yong *et al.* (2002) studied the palladium absorption capacity of the *Desulfovibrio desulfuricans* NCIMB 8307. This has happened either in the presence or absence of an electron donor, which can determinate assignment of the metal biosorbtion of Pd (II) and bioreduction of Pd (II) to Pd (0). The maximum rate of biosorption to pH 2 was 196 mg Pd / g cellular dry weight (1.85 mmol / g; about 20% of the dry mass). In less than 10 minutes biosorption of palladium has reached its maximum of 85%, and the biomass was fed in 30 minutes.

The strain *Bacillus sphaericus* JG-A12 was isolated of Pollmann *et al.* (2016) from a uranium mine and was identified that has the ability to accumulate high amounts of uranium, cadmium, aluminum, cadmium, gold, copper and critical metals such as palladium and platinum. Creamer *et al*. (2006) studied bacterium *Desulfovibrio desulfuricans* ability to recover gold and palladium from scrap leaching and electronic waste. Thus, the Au(0) precipitates extracellular. The presence of high concentrations of copper in the leachate inhibited dehydrogenase-mediated removal of Pd (II), but in the absence of copper facilitates the removal of more than 95% thereof. Palladium can be biorecovered from aquatic environments through the use of sludge, fixed foam, rich in *Serratia sp.* or by bioreduction of sodium tetrachloro-palladate with *Anabaena*, *Bacteroides vulgatus*, *Bacillus sphaericus*, *Calothrix*, *Clostridium pasterianum*, *Cupriavidus metallidurans*, *C. nector*, *Citrobacter braakii*, *Delsulfovibrio fructosivorans*, *D. vulgaris*, *Paracoccus denitrificans*, *Pseudmonas putida*, *Plectonema boryanum*, *Geobacter sulfurreducens* and *E.coli* (Zhuang *et al.*, 2015; Nancharaiah *et al.*, 2016).

The platinum is converted from the platinum chloride by *D. sulfuricans*, *Pseudomonas sp*., dysprosium is bioaccumulated by *Penidiella sp.* T9 and bioabsorbed by *P. aeruginosa*, the lanthanum is bioabsorbed by *Pseudomonas aeruginosa*, *Bacillus subtilis*, *Myxococcus xanthus*, *Myxococcus smegmatis*, *E. coli*, *Pseudomonas sp*., neodymium by *P. aeruginosa*, scandium by *Saccharomyces cerevisiae*, *Rhizopus arrhizus*, *Aspergillus terreus*, europium by *P. aeruginosa*, *Myxococcus xanthus* and yterbiul by *M. smegmatis* (Braud *et al*., 2009; Nancharaiah *et al.*, 2016).

According to Nancharaiah *et al.* (2016), by the bioreduction process, the silver nitrate is converted into silver by *Aeromonas spp*. SH10, *Bacillus cereus*, *Bacillus subtilis*, *B.megaterium*, *B. licheniformis*, *Brevibacterium casei*, *Corynebacterium* spp. SH09, *Enterobacter cloacae*, *Escherichia coli*, *Klebsiella pneumonia*, *Lactobacillus fermentum*, *Proteus mirabilis*, *Pseudomonas putida*, *P. stutzeri* and *Serratia nematodiphila*.

The Pt recovery potential of halophilic mixed cultures in acidic saline conditions was demonstrated. Halophilic mixed cultures (main taxonomic families present: *Halomonadaceae*, *Bacillaceae* and *Idiomarinaceae*) were employed for the biorecovery of platinum (Pt). Halophilic bacteria were enriched from *Artemia cysts*, living in salt lakes. The halophilic cultures were able to recover > 98% Pt(II) and > 97% Pt(IV) at pH 2 within 3–21 h (4–453 mg Pt /h g biomass was recovered) (Maes *et al*., 2016).

Penicillium tricolor has the ability to synthesize large quantities of citric acid containing three carboxyl groups and one hydroxyl, which may form stable chelates with trivalent rare earth elements (Zhuang *et al.*, 2015).

In 2011, Sturm *et al.* have isolated and identified a strain of *Leucobacter chromiiresistens* resistant to chromium. Another species resistant to high concentrations of chromium is *Clostridium chromiireducens* (Inglett *et al*., 2011). *Saccharomyces cerevisiae* and *Aspergillus niger* are capable to biosorbtion of the chromium from the copper electroplating effluents and the waste water produced by this process (Wang *et al*., 2006). Also, the chromium may be recovered by *Bacillus sp*., *Mucor meihi* and *Cunninghamella elegans* from tannery effluents and waste water generated by the process itself (*Prigioni et al., 2009; Vijayaraghavan et al., 2015*).

Proteus vulgaris is able to absorb the cobalt, with a high efficiency under conditions of neutral pH and *Saccharomyces cerevisiae* can accumulate cadmium and cobalt. (Neyland *et al.*, 1952; Norris, 1977).

Nitrosomonas sp., *Actinobacteria sp.*, *Propionibacterium spp.*, *Sphingobacteria sp.* and *Corynebacterium spp.*, are bacterial genera involved in removing beryllium from contaminated aquatic environments (Sun *et al.*, 2012). Gomez *et al.*, (1999) have studied the ability of two bacteria capable of oxidizing iron and sulfur, *Thiobacillus ferrooxidans* and *T. thiooxidans* and to solubilize a number of heavy and / or critical metals. Thus, it has been shown that, depending on the culture medium, contaminant and the soil sample, these two bacteria are solubilized 50% from the quantity of the arsenic, cadmium, cobalt, chromium, copper, nickel, vanadium, zinc, beryllium and boron.

It was demonstrated the removed and partially recovered of the ruthenium contained in industrial effluents by using the bacteria *Rhodopseudomonas palustris* as biosorbents. The bacteria tested have adsorbed around 40 mg/g dry biomass of the ruthenium. The amount of ruthenium recovered from the biomass ranged from 42 % to 72 % of that adsorbed by bacteria (Colica *et al.*,2012).

Biorestoration (restoring the original status or a state close to the original by using living organisms) environments rich in antimony can be performed using bacteria belonging to the *Bacillus*, *Haemophilus*, *Micrococcus* genera, or *Gallionella ferrugiinea*, *Bacillus pumilus*, *Leptothrix ochracea*, *Pseudomonas aeruginosa* species. Another process which can be exploited antimony is bioprecipitation with *Desulfovibrio desulfuricans* able to perform this role. The antimony can be immobilized using chemolithotrophic, acidophilus bacteria or belonging to the family *Geobacteraceae*. Microorganisms are used as adsorbents *Rhizopus arrhizus* of antimony, *Microbacterium arabinogalactanolyticum*, *Pseudomonas aeruginosa*, *Pseudomonas fluorescens*, *Neocosmospora sp.*, *Rhizopus sp.*, *Trichoderma sp.* (Mubarak et al., 2015). *Skermanella stibiiresistens* is a bacterium that has the ability to assimilate antimony. In 2012, Luo *et al.* isolated the strain SB22T from a coal mine.

The ferric iron reduction mediated by *Acidithiobacillus thiooxidans* can be applied to an aerobic reductive dissolution of nickel laterite tailings. Aerobic reductive dissolution using a consortium of *Acidithiobacillus thiooxidans* and *Acidithiobacillus ferrooxidans* extracted similar amounts of nickel and cobalt in only 7 days as anaerobic reductive dissolution using *Acidithiobacillus ferrooxidans* (Marrero et al., 2015).

CONCLUSIONS:

Microorganisms interact with metals thus altering their physical and chemical condition. Isolation of individual strains and identification of microbial consortia that can be used in the design and development of effective biotechnological processes for the extraction of high-tech critical metals is a current challenge of the scientific research in Europe. The number of studies on interactions between microorganisms and the most critical metals is too low. Even though the biotechnology of removing metal contaminants from different sources is advanced, the research for finding technological solutions for the recovery of high-tech critical metals is still at the beginning. Scientific studies on the functional responses of microbial consortia to specific metals and new characterized microorganisms with potential to be applied in biosolubilization, biomineralization and bioaccumulation will be essential for assessing the potential role of microbial communities in the biorecovery of high-tech critical metals from mine tailings.

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* Communication from the commission to the European parliament, the council, the European economic and social committee and the committee of the regions tackling the challenges in commodity markets and on raw materials /* COM/2011/0025 final */, http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:52011DC0025

** Communication from the commission to the European parliament, the council, the European economic and social committee and the committee of the regions On the review of the list of critical raw materials for the EU and the implementation of the Raw Materials Initiative /* COM/2014/0297 final */, http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:52014DC0297