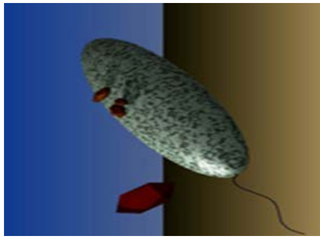

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BRATISLAVA 27 –29 MAY 2015

MECHANISMS OF INTERACTION BETWEEN TRACE ELEMENTS AND MICROORGANISMS IN THE COMPLEX BIOTIC/ABIOTIC SYSTEMS (BIOSORPTION AND BIOACCUMULATION)

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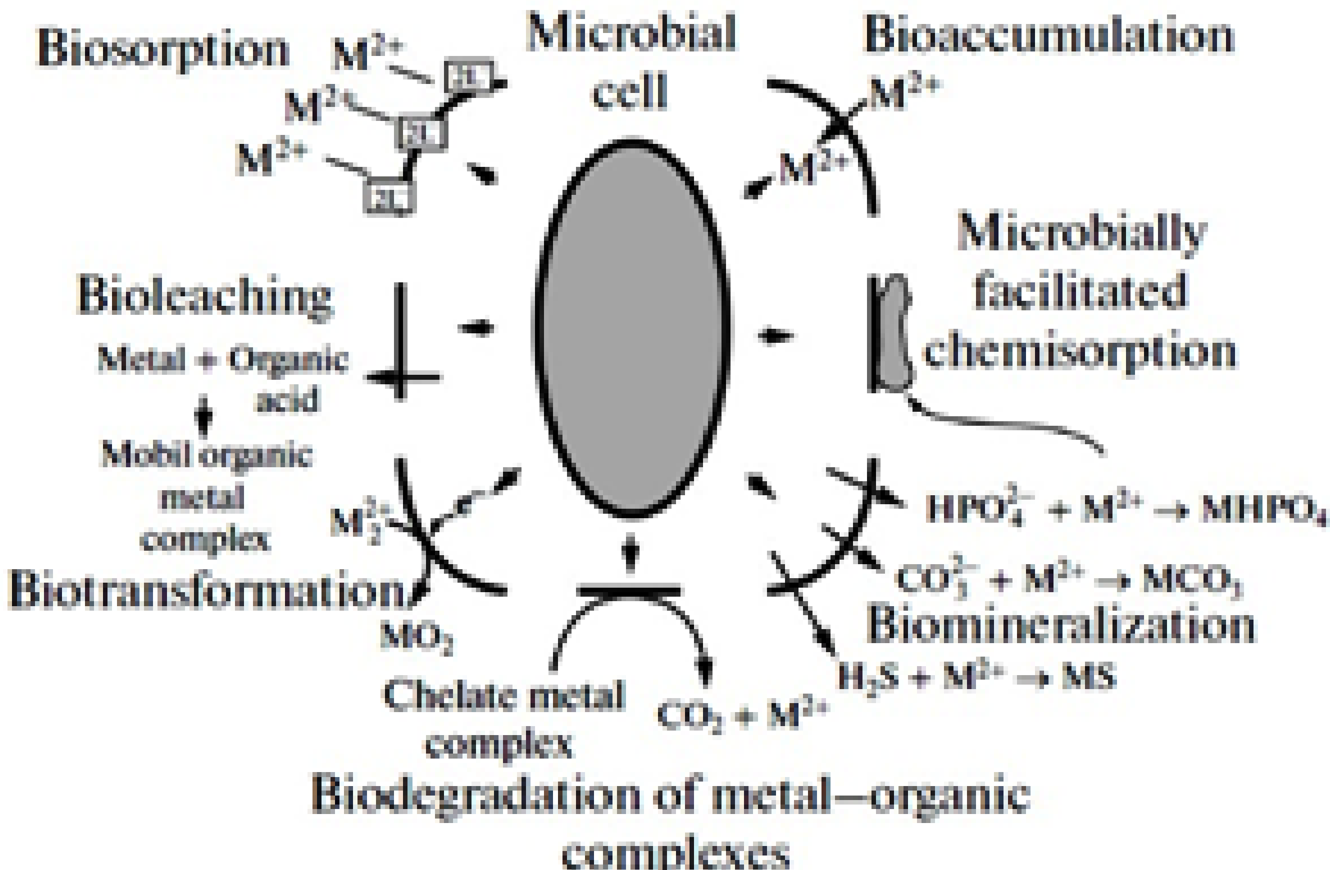
Theoretical aspect:

Microorganisms are among the important components in complex bio-mineral systems (soils, grounds, natural waters etc.), which influence the biogeochemical cycles of elements (Perelomov et al., 2013).

Practical aspect:

Microorganisms, their products and their residues can be used in the techniques of wastewater treatment and for immobilization of trace elements in soils (Volesky and Holan, 1995; Gadd, 2008).

Main processes of interaction of microorganisms with trace elements (Tabak et al., 2005)



Definitions:

Biosorption is the complex of the processes that occur on the surface of cell walls and the plasmalemma through mechanisms of ionic exchange, adsorption, complex and chelate formation, and microprecipitation (Guibal et al., 1992).

Bioaccumulation is the process of the biological absorption of elements by living cells, followed by accumulation in the cytoplasm (Perelomov et al., 2013).

Comparison of the features of biosorption and bioaccumulation (Vijayaraghavan, Yeoung-Sang Yun, 2008)

Features	Biosorption	Bioaccumulation
Cost	Usually low. Most biosorbents used were industrial, agricultural and other type of waste biomass. Cost involves mainly transportation and other simple processing charges.	Usually high. The process involves living cells and; hence, cell maintenance is cost prone.
pH	The solution pH strongly influences the uptake capacity of biomass. However, the process can be operated under a wide range of pH conditions.	In addition to uptake, the living cells themselves are strongly affected under extreme pH conditions.
Temperature	Since the biomass is inactive, temperature does not influence the process. In fact, several investigators reported uptake enhancement with temperature rise.	Temperature severely affects the process.
Maintenance/storage	Easy to store and use	External metabolic energy is needed for maintenance of the culture.
Selectivity	Poor. However, selectivity can be improved by modification/processing of biomass	Better than biosorption
Versatility	Reasonably good. The binding sites can accommodate a variety of ions.	Not very flexible. Prone to be affected by high metal/salt conditions.
Degree of uptake	Very high. Some biomasses are reported to accommodate an amount of toxicant nearly as high as their dry weight.	Because living cells are sensitive to high toxicant concentration, uptake is usually low.
Rate of uptake	Usually rapid. Most biosorption mechanisms are rapid.	Usually slower than biosorption. Since intracellular accumulation is time consuming.
Toxicant affinity	High under favorable conditions.	Depends on the toxicity of the pollutant.
Regeneration and reuse	High possibility of biosorbent regeneration, with possible reuse over a number of cycles.	Since most toxicants are intracellularly accumulated, the chances are very limited.
Toxicant recovery	With proper selection of elutant, toxicant recovery is possible. In many instances, acidic or alkaline solutions proved an efficient medium to recover toxicants.	Even if possible, the biomass cannot be utilized for next cycle.

Biosorbents:

Biosorbents for the removal of trace elements come under the following categories: bacteria, fungi, algae, industrial wastes, agricultural wastes and other polysaccharide materials. In general, all types of biomaterials have shown good biosorption capacities towards all types of ions.

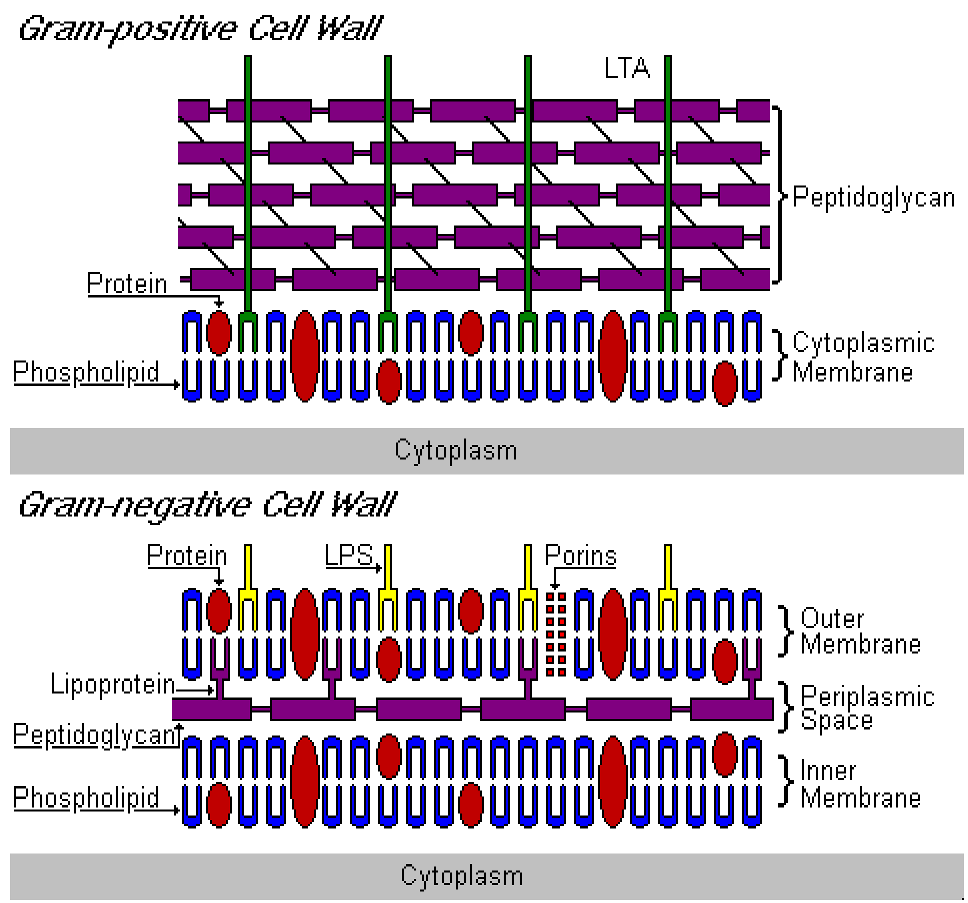
Biosorbents:

Biosorption processes are determined by two main factors, such as:

- the surface properties of the cell membrane (charge, quantity and orientation of the metal-binding functional groups);
- the chemical forms of the metal compounds in the liquid phase.

Biosorbents:

Gram-positive bacteria have a larger sorption capacity, due to the thick peptidoglycan layer of the cell walls, which contain numerous sorption positions (Beveridge, 1989).

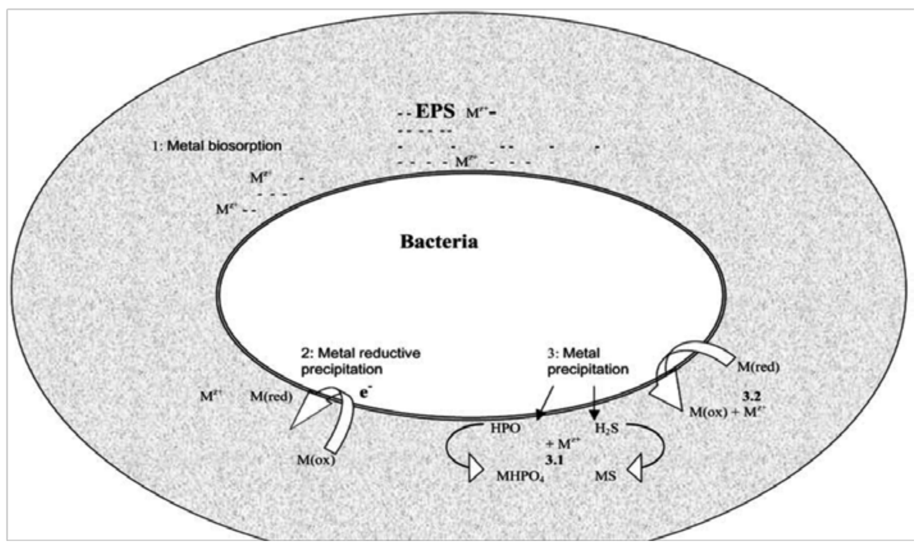


Biosorbents:

Bacteria	Metal ions concentration at biomass [μM]								
	Na	K	Mg	Ca	Mn	Fe	Ni	Cu	Ag
Bacillus subtilis **(Gram +)**	2.7	1.9	8.2	1.4	0.8	3.4	1.1	2.9	0.3
Bacillus licheniformis **(Gram -)**	0.9	0.5	0.4	0.6	0.7	0.7	0.5	0.5	0.03

Biosorbents:

Microorganisms produce extracellular polymeric substances (EPS). EPS can be held by cells and form of capsules, or they may be separated and form a slime. Typically in the EPS polysaccharides and proteins are included and often they accompanied by the nucleic acids, lipids and humic substances (Flemming and Wingender, 2001)



Biosorbents:

Potent metal biosorbents under the class of bacteria include *Bacillus* (Nakajima and Tsuruta, 2004; Tunali et al., 2006), *Pseudomonas* (Chang et al., 1997; Uslu and Tanyol, 2006) and *Streptomyces* (Mameri et al., 1999; Selatnia et al., 2004a), *etc*.

Important fungal biosorbents include *Aspergillus* (Kapoor and Viraraghavan, 1997; Jianlong et al., 2001; Binupriya et al., 2006), *Rhizopus* (Bai and Abraham, 2002; Park et al., 2005) and *Penicillium* (Niu et al., 1993; Tan and Cheng, 2003), *etc*.

Adsorption models:

- Langmuir model is based on the assumption that the maximum adsorption occurs when the surface of the adsorbent presents saturated monolayer of solute molecules and the adsorption energy is constant, and that there is no migration of adsorbate molecules in the surface plane.
- Freundlich model based on empirical data and has been designed for heterogeneous surfaces.
- Brunauer, Emmett and Teller (BET) isotherm is a multilayer adsorption on heterogeneous sites with different binding affinity and suggests that the Langmuir isotherm describes the processes in each layer (Morley and Gadd, 1995).

Use of models to describe metal accumulation by microorganisms (Ledin, 2000)

Organism	Metal	Model	Reference
Pseudomonas putida; *Escherichia coli*	Hg(II)		Aller et al., 1996
lyophilized cells		"Anti-Langmuirian shape"	
living cells		Freundlich, Langmuir	
Pseudomonas EPS 5028	U	Freundlich	Pons and Fusté, 1993
Pseudomonas aeruginosa	Hg(II)	Followed Langmuir more closely than Freundlich	Chang and Hong, 1994
Pseudomonas aeruginosa	U	Langmuir	Hu et al., 1996
Pseudomonas cepacia	Cd(II), Zn(II)	Langmuir	Savvaidis et al., 1992
Bacillus subtilis, *Micrococcus luteus*.	UO_2^{2+}, Cd(II), Zn(II), Cu(II)	Langmuir	Cotoras et al., 1992
Bacillus cereus, *Bacillus subtilis*, *Escherichia coli*, *Pseudomonas aeruginosa*	Ag(I), Cd(II), Cu(II), La(III)	Freundlich	Mullen et al., 1989
Zoogloea ramigera	Pb(II), Ni(II), Cu(II), Fe(III)	Freundlich, Langmuir	Sag and Kutsal, 1995a
Zoogloea ramigera	Cu(II)	Freundlich	Aksu et al., 1992
Thiothrix strain A1	Cu	Freundlich	Shuttleworth and Unz, 1993
	Zn(II), Ni(II)	Biphasic Freundlich	
Rhodococcus erythropolis			
living cells	Zn(II), Cd(II)	NICA	Plette et al., 1996c
isolated cell walls	Ca(II), Cd(II), Zn(II)	NICA	Plette et al., 1996a
Consortia of denitrifying bacteria	Cr(VI)	Langmuir	Guan et al., 1993
Synechocystis sp.; *Synechococcus* sp.; *Plectonema boryanum*; *Anabaena variabilis*; *Oscillatoria* sp.	TcO_4^-	Freundlich; bi-phasic Scatchard	Garnham et al., 1993a
Chlorella vulgaris	Cu(II)	Freundlich	Aksu et al., 1992
Dunaliella tertiolecta	Pb(II)	Langmuir (one-site and two-site model), curved Scatchard	Santana-Casiano et al., 1995

Factors affecting biosorption:

- Properties of biomass
- Solution pH
- Ionic strength
- Temperature
- Biosorbent dosage
- Biosorbent size
- Initial solute concentration
- Agitation rate

Solution pH

Most organic functional groups on the cell surface are amphoteric. The ionization of functional groups in the cell wall provides an electrical charge at the bacterium's surface.

- Organic acid:

  $R\text{-}COOH \rightarrow R\text{-}COO^- + H^+$

- Hydroxyl group:

  $R\text{-}OH \rightarrow R\text{-}O^- + H^+$

- Phosphate group:

  $R\text{-}PO_4H_2 \rightarrow RPO_4H^- + H^+$

At low pH, microbial surfaces carry a net positive charge while with increasing pH the net charge turns negative. The pH at which the total number of positive charges equals the number of negative charges is referred to as the point of zero charge (PZC). Bacterial cells have a PZC in the region of pH 1.75–4.15 (Wicken, 1985).

Ionic strength

The ionic strength can influence metal accumulation by affecting the activities of the metal ions in solution, as well as the surface charge and double-layer capacitance of the hydrated cells (Santana-Casiano et al., 1995)

Selectivity of sorption

Some types of microorganisms could accumulate a broad range of metals with no specific priority, while others are specific for certain types of metals.

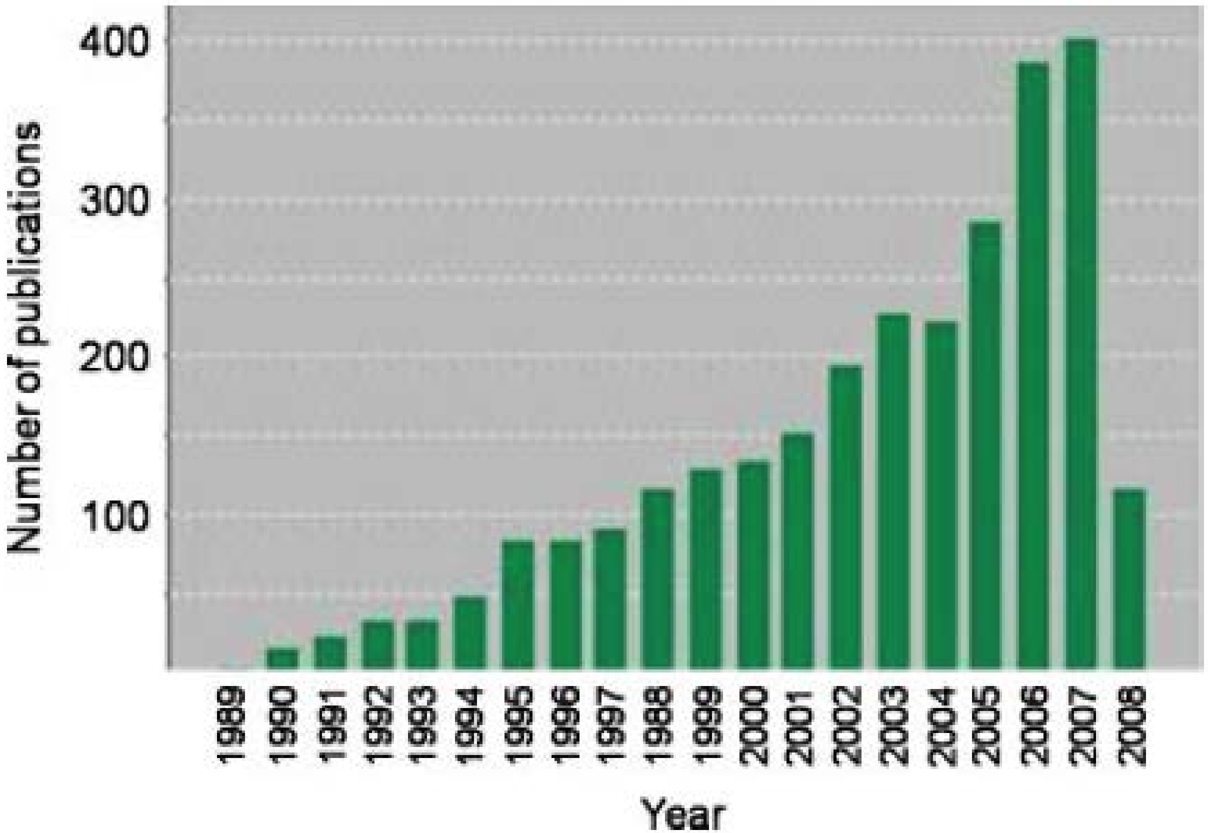
RedOx conditions

The oxidized forms of U, Pd, Se, Tc, Mo, Cr, and others are well dissolved in aqueous media and more mobile in aerobic groundwater compared with reduced forms of these elements (Perelomov and Chulin, 2014). The oxidized forms of trace elements in solution are represented mainly by anions; therefore, they are usually weakly sorbed on negatively charged surfaces. Reduction leads in general to the formation of sedentary precipitation (oxides, hydroxides, etc.).

Principle advantages of biological technologies:

- biological processes can be carried out in situ at the contaminated site;
- bioprocess technologies are usually environmentally benign (no secondary pollution);
- they are cost effective.

Numbers of papers appearing with 'biosorption' in the topic as listed in the ISI Web of Science database (Gadd, 2008)



Ternary systems

Much of the current researches have focused on the physicochemical interactions between trace elements and biotic and abiotic components, and little investigation has been directed toward the **triple interaction** between trace elements, minerals and the biota (or products of its metabolism).

For these purposes special ternary **BIO-MINERAL** and **ORGANO-MINERAL SYSTEMS** may be constructed (Perelomov, Kandeler, 2006; Perelomov, Yoshida, 2008; etc)

Thank you!