MICROBIAL PROCESSES IN THE REMOVAL OF TOXIC METALS AND RADIONUCLIDES FROM THE ENVIRONMENT

Prof. K. Sivakumar

Department of Plant Sciences, School of Biological Sciences,

Madurai Kamaraj University, Madurai – 625021

Email: kshivam69@gmail.com

ABSTRACT

The increasing amount of toxic metals and radionuclides emitted into the biosphere as a result of industrial activities indicate a potential hazard to the ecosystem. With the increasing need for the safe removal of toxic metals and radionuclides and the continued public interest of environmental problems, the microbial processes play an important role in the future of waste management. The key microbial processes which may effect mobilisation or immobilisation of toxic elements are reviewed.

Key words: Biosorption, bioprecipitation, bioaccumulation, siderophores, toxic metals, radionuclides

INTRODUCTION

Rapid industrialisation and urbanisation have resulted in elevated emission of toxic heavy metals and radionuclides entering the biosphere. An inorganic toxicant may be cationic such as metallic ions of mercury, cadmium, chromium, lead, nickel and uranium, etc. Toxic inorganic may also be alkylated or aromatized forms of metal ions such as methyl-mercury and phenyl-mercury. Heavy toxic metals and radionuclides seriously influence the metabolism of living organisms and cause permanent threatening of health. The increasing amounts of toxic metals emitted into the biosphere as a result of industrial activities indicate potential hazard to ecosystem. Solid and/or liquid wastes containing toxic heavy metals may be generated in various industrial processes, e.g., in chemical manufacturing, electric power generating, coal and ore mining, melting and metal refining, metal plating, and others. Domestic waste sludge may also contain undesirable level of toxic metals. The biosorption of copper is studied using *Sargassum wightii*, which is a biomass of marine brown alga, brown seaweed *S. wightii* can be recommended for the removal of copper from the industrial effluents (Sivakumar and Anbazhan, 2004). The heavy metals such as cadmium arsenic bismuth, copper, zinc, chromium, cobalt, selenium, etc., contaminate the envionrment. Environmental pollution due to Cu arises from industrial and agricultural emissions. Eventhough the literature present papers using algal cells (Schmitt et al., 2001) and other biomaterials (Lister and Lime, 2001; Schmeider et al., 2001). Little is known about the behavior of a continuous system for this kind of treatment. The purpose of the present study was to investigate the behavior of continuous serial reaction for the uptake of copper. The brown seaweed, *Sargasum* is made up of polysaccharides alginate, usually Calcium and Sodium with a high potential for the accumulation of heavy metals, as compared to other algae (da Costa and de Franca, 1996). The polysaccharides are produced due to the interaction between alginic acid, alkaline and alkaline-earth elements from sea water.

The biosorption of copper on *Padina gymnospora* was investigated in a batch system. The relationship between the response and the independent variables was developed via the quadratic approximating function of copper sorption capacity of sorbent from this study, it can be concluded that the copper can be removed by using a brown alga *P. gymnospora*, which is abundant are chiefly available alga. Dry biomass of *P. gymnospore* proves to be cost effective an efficient to eliminate heavymetal especially copper for aquatic effluents and the process is feasible reliable and eco-friendly. This brown alga can be recommended for the removal of copper from the industrial effleuncs (Murugaiyan and Sivakumar, 2022).

Aqueous effluents that are produced during nuclear power and defence activities frequently contain radionuclides (Faisen et al., 1990). These effluents derive from various sources, including reactor coolant water, evaporator condensate, and fuel reprocessing waste. Metals contained within these wastes include the fission product strontium and caesium. Removal of radionuclides is a critical element of the treatment of nuclear industry effluents. ^{90}Sr poses a particular health hazard because of its tendency to be incorporated into bone. The chemical behaviour of ^{137}Cs mimics that of sodium and potassium, which are readily absorbed by cells.

Conventional techniques to remove toxic metals and radionuclides, e.g., ion exchange and precipitation, lack specificity and are ineffective at low concentrations of metal ions.

Environmental biotechnology is the technology of applying mainly microorganisms to improve the quality of the environment. Bioremediation is the use of living organisms to reduce or eliminate environmental hazards resulting from the accumulation of toxic chemicals and other hazardous wastes. This technology is based on the utilisation of naturally occurring or genetically engineered microorganisms to transform organic and inorganic compounds. Biological methods compete with physical and chemical technologies. For an economical biological process of remediation and elimination of toxic metal contaminants, the following features are essential: inexpensive biomass, high metal binding capacity, selective metal binding, effective desorption methods, recycling of desorbents, and repeated use of biomass.

Microbial transformation of toxic metals and radionuclides may affect their solubility, mobility, and bioavailability (Francis, 1997). Several of the key microbial processes may affect mobilisation or immobilisation of toxic elements by one or more of the following mechanisms:

- chelation of elements by metabolites,
- oxidation-reduction of metals which affect the solubility or valence state,
- changes in pil which affect the ionic state,
- biosorption by functional groups on the cell surface,
- bioaccumulation by an energy-dependent transport system,
- immobilisation due to formation of stable materials,
- biomethylation,

- biodegradation of organic complex of metals and radionuclides.

The major ways of mobilisation or immobilisation are delineated in Fig. 1.

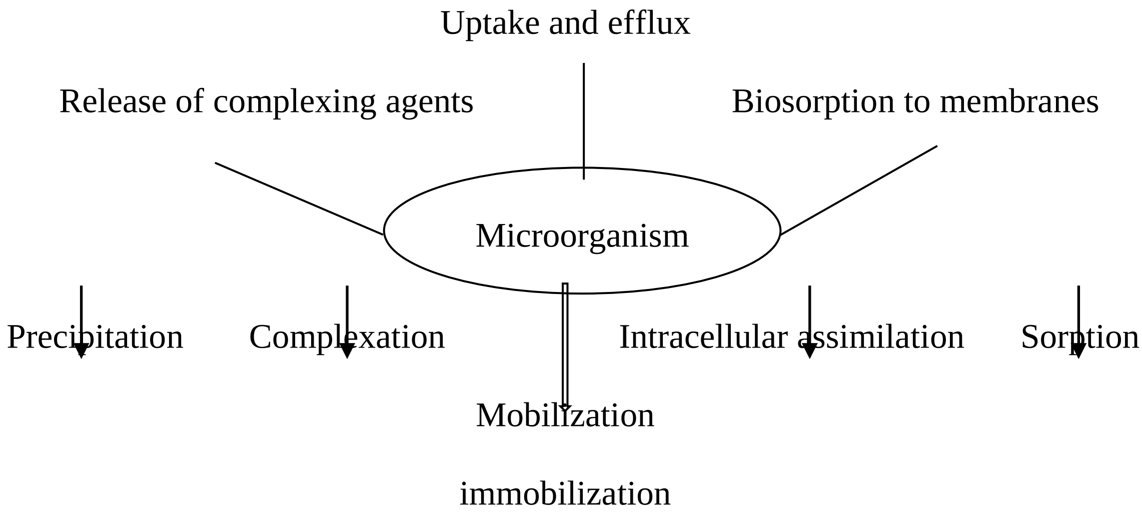

Fig. 1. Metal processing mechanisms of microorganisms

Fundamental information on mechanisms and potential application of biotechnology have been discussed by Mullen et al. (1989), Beveridge and Doyle (1989), Ashly and Roach (1990), Francis (1990), Volesky (1990), Brierley (1991), and Ehrlich (1994).

There is a wide variety of microorganisms, including bacteria, fungi, yeast, and algae that can interact with metals and radionuclides through several mechanisms to transform them (Poole and Gadd, 1989) (Table I).

Table 1. Examples of toxic heavy metals accumulating microorganisıms

Organism	Element
Citrobacter sp.	Lead, Cadmium
Thiobacillus ferrooxidans	Silver
Bacillus cereus	Cadmium
Bacillus subtilis	Chromium

Pseudomonas aeruginosa	Uranium
Micrococcus luteus	Strontium
Rhisopus arrhizus	Mercury
Aspergillus niger	Thorium
Saccharomyces cerevisiae	Uranium

1. MOBILISATION

Dissolution of toxic metals and radionuclides is due to oxidation-reduction reaction and production of mineral or organic acid metabolites, as well as lowering of the pH.

1.1. Enzymatic oxidation

Inorganic compounds that can exist in more than one oxidation state and in which the higher oxidation state is less soluble, enzymatic oxidation may be a useful way for removing the inorganic species from solution. Much of the available information on the dissolution of metais deals with the ore leaching by autotrophic microorganisms such as Thiobacillus ferrooxidans, T. thiooxidans. The role of Thiobacillus ferroaxidans in the removal of uranium from ore is due to indirect and direct actions.

Indirect action:

$UO_2 + 2Fe^{3+} \rightarrow UO_2^{2+} + Fe^{2+}$

Direct action:

$UO_2 \rightarrow UO_2^{2+}$

Ferrous iron thus produced is a carrier for electrons for uranium oxidation and is reoxidized by Thiobacillus ferrooxidans:

$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O$

1.2. Enzymatic reduction

In case of inorganic compounds that can exist in more than one oxidation state and whose reduced state is insoluble, enzymatic reduction may be useful in removing the species from solution. Enzymatic reduction by facultative and obligate anaerobic microorganisms may be a potential application of in situ bioremediation.

Examples of bacterial reduction:

$UO_2^{2+} \rightarrow UO_2$

$Fe^{3+} \rightarrow Fe^{2+}$

$Mn^{4+} \rightarrow Mn^{2+}$

1.3. Complexation

The use of complexation agents may be useful in mobilizing toxic inorganic compounds to facilitate their removal from solid waste (Birch and Bachofen, 1990).

Complexes can be represented as follows:

$$\text{Metal} + \text{Ligand} \Leftrightarrow \text{Metal complex}$$

Microbial complexing agents can be low molecular weight organic acids and alcohols, high molecular weight ligands, siderophores, and toxic metal binding compounds. Low molecular weigh compounds as various organic acids (citric acid, tricarboxylic acids) released during microbial degradation have been found to have metal complexation ability. Some amino acids formed by bacteria can also be complexing agents. The rank order of the complexing ability of organic acids:

Tricarboxylic acids > dicarboxylic acids > monocarboxylic acids

The microbial degradation of organic compounds, mainly cellulose and lignin, releases large macromolecular compounds. They are differentiated into three fractions: compounds soluble in alkali as humic acids, compounds soluble in acids as fulvic acids, and residual humic fraction that cannot be extracted by either dilute alkali or acid. These macromolecules are termed humates. Their structures have not yet been fully characterized, although certain functional groups, such as carboxyl, alcohol, and phenol are common to all humic macromolecules. The complexation of heavy metals and radionuclides to humates is highly pH-dependent.

1.4. Siderophores

When microorganisms are grown in an iron deficient medium, they produce specific iron chelators, so called siderophores, in the medium. They play an important role in the complexation of toxic metals and radionuclides and increase their solubility (Neilands, 1983). Siderophores are compounds that possess catecholate, phenolate or hydroxamate as their binding groups. Over the past few years many siderophore or siderophore-like compounds have been identified from various biological systems. Although siderophores are primarily specific for Fe(III), they can also complex other metals and radionuclides.

2. IMMOBILISATION

Immobilisation of toxic metals and radionuclides are brought about by precipitation, biosorption and bioaccumulation. These processes have received considerable attention because of their potential application of waste water treatment containing toxic metals and radionuclides.

2.1. Precipitation

Sulfate reduction is an example for the precipitation of metallic ions in solution. Most metal sulfides are quite insoluble in aqueous solution. The stability of these sulfides depends on the maintenance of anoxic conditions. Sulfate reducing bacteria are being used in engineered natural systems such as constructed wetland to treat metal contaminants. Microbial degradation of organo-phosphates to ortho-phosphate can lead to metal precipitation throught formation of metal-phosphates, especially above pH 7. Intracellular phosphates may also immobilise metals.

2.2. Biosorption

Biosorption of toxic metals and radionuclides is based on non-enzymatic processes such as adsorption (Fig. 2). Adsorption is due to the non-specific binding of ionic species to cell surface-associated or extracellular polysaccharides and proteins (Mullen and et al. 1989; Volesky, 1990). Bacterial cell walls and envelopes, and the walls of fungi, yeasts, and algae are efficient metal biosorbents that bind charged groups. The cell walls of Gram-positive bacteria bind larger quantities of toxic metals and radionuclides than the envelopes of the Gram-negative bacteria. Bacterial sorption of some metals can be described by the linearised Freundlich adsorption equation,

$$\log S = \log K + n \log C$$

where S is the amount of metal absorbed in μmo.g-1, C is the equilibrium solution concentration in $\mu mol.l^{-1}$, K and n are the Freundlich constants (Mullen et al. 1989). Metallic ions can be removed by alive or dead biomass. Biosorbents may be regenerated by treatment with acid or with certain chelating agents. Besides of bacteria, waste fungal biomass deriving from several industrial fermentations may provide an economical source of biosorptive materials. Many species have high cell wall chitin contents, and this polymer of N-acetyl-glucosamine is an effective biosorbent.

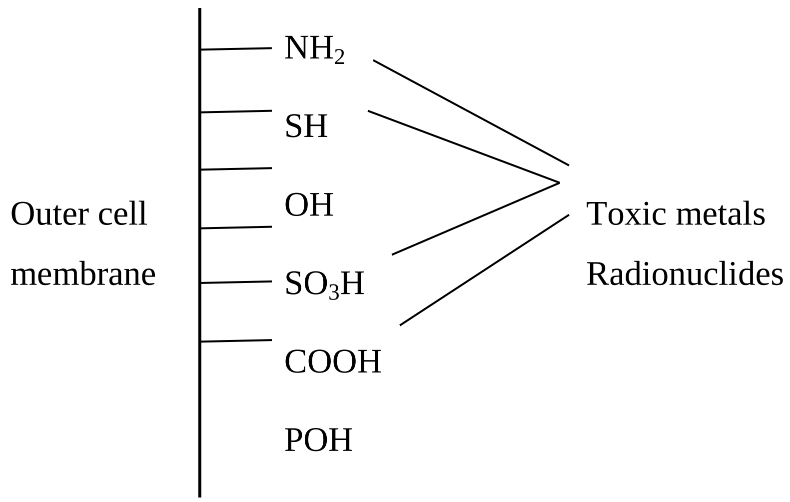

Fig. 2. Sites of biosorption of toxic metals

Chitosan and glucans also have a significant biosorptive capacity. Biosorption is used in Dioremediation of toxic metal and radionuclide waste streams. The two-step biosorption process can be seen in Fig. 3.

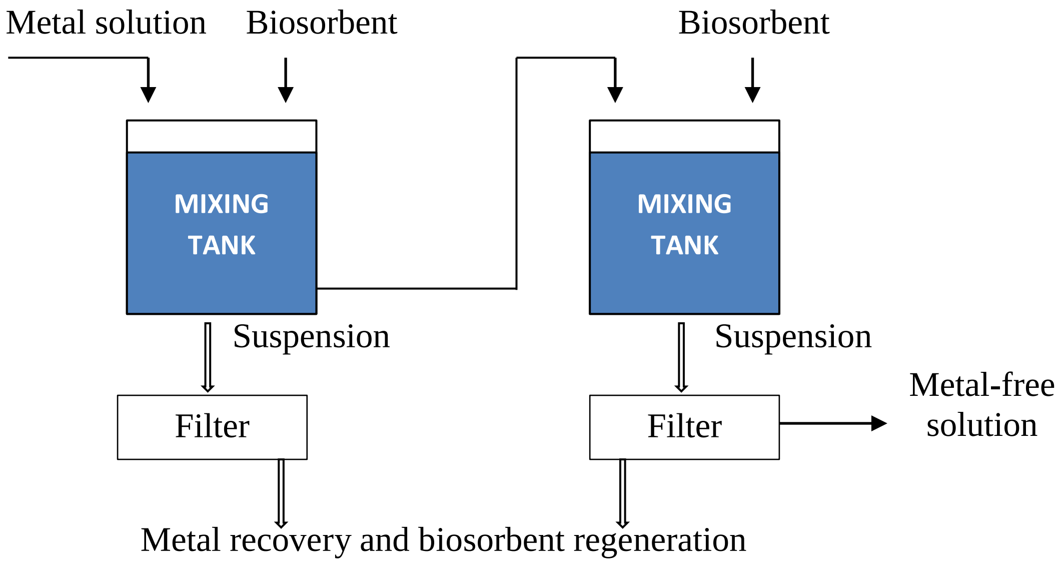

Fig. 3. Two-stage biosorption process

2.3. Bloaccumulation

Bioaccumulation has been described for such metals as mercury, lead, silver, cadmium, nickel, ^{137}cesium, ^{60}cobalt, ^{85}stroncium, plutonium, and uranium. Intracellular accumulation of toxic elements is carried out by an energy dependent transport system (Gadd, 1988).

Potential mechanisms of toxic metal flux across membranes can be ion pumps, ion channels, carrier mediated transport, endocytosis, complex permeation, and lipid permeation.

Permeabilization of cell membranes to toxic elements can result in further exposure of intracellular metal binding sites and increase passive accumulation. The most widely used living cell system is capable to remove toxic metals from effluents of waste water treatment. The metals and radionuclides are released inside the cells, incorporated into biochemical pathways, or trapped in an inactive form by complexation with another high affinity ligand.

Heavy metal pollution has become one of the most serious environmental problem in the recent years. Presence of heavymetals even in traces is toxic and detrimental to both flora and fauna. Metals can be distinguished from other toxic pollutants. Since they are non-biodegradable and can accumulate in the living tissues, thus becoming concentrated throughout the food chain. The expanding technological activities have especially accelerated the addition of numerous poisonous metal pollutants to the environment resulting in their immobilization and accumulation in various microbial ecosystem and even threatending human life (Volesky, 1992).

The major source of metals into the environments is through discharges from industries such as allow, pigments, tannery, fertilizers, pesticides, pharmaceuticals, chemicals etc. Heavy metal modify the structures and productivity of aquatic ecosystem. Though heavy metals are essentially needed by living organism from various metablic process (Whitton and Say, 1975), their excess concentration showed lethal effects. The physiological as well as toxicological effects improved by metal irons are considered to be biological continum. Since algae are considered to be basic in food chain as a primary producer.

CONCLUSION

The potential application of biotechnology for the treatment of various forms of toxic solid and liquid wastes has advantages and disadvantages. The advantages of microbial treatment are: environment friendliness, self-reproducibility, adaptability, recyclisation of bioproducts, specificity, and good cost/benefit ratio. The disadvantages include the slowness of the processes, and the difficulty to control the processes.

However, due to the increasing need for the safe removal of toxic metals and radionuclides and the continued public interest to environmental problems, the microbial processes may play an important role in the future of waste management. Commercial utilization of these tools is rare, but the development of these topics of biotechnology is desirable on both environmental and economic aspects.

References

Ashly, N. V. and Roach, D. J. W. (1990). "Review of biotechnology application to nuclear waste treatment." J. Chem. Tech. Biotechnol. 49:381-3944.

Beveridge, T. J. and Doyle, R. J. (1989). Metal Ions and Bacteria. John Wiley Sons, New York.

Brierley, C. L. (1991). "Bioremediation of metal-contaminated surface and ground-waters." Geomicrobiology 8:201-223.

Birch, L. and Bachofen, R. (1990). "Complexing agents from microorganisms." Experientia 46:827-834.

da Costa, A.C.A. and de Franca, F.P. (1996). Cadmium uptake by biosobent seaweeds: Adsorption isotherm and some process conditions. Separation Science and Technology, 31: 2373-2393.

Ehrlich, H. L. (1994). "Inorganic hazardous waste amenable to biological transformation." In: Biotechnology for the Treatment of Hazardous Waste (D. L. Storner, ed.). Lewis Publishers, Boca Raton-Ann Arbor-London-Tokyo, pp. 27-44.

Lister, S.K. and Line, M.A. (2001). Potential utilization of sewage sludge and paper mill waste for biosorption of metals from polluted water ways. Bioresource Technology, 79: 35-39.

Faison, B. D., Cancel, C. C., Lewis, S. N., and Adler, H. I. (1990). "Binding of dissolved strencium by Micrococcus luteus." Appl. Environ. Microbiol. 56:3649-3656.

Francis, A. J. (1990). "Microbial dissolution and stabilization of toxic metals and radionuclides in mixed wastes." Experientia 46:840-851.

Francis, A. J. (1997). "Biotechnology of radicactive wastes: a general overview." In: Biotechnology for Waste Management and Site Restoration (C. Ronneau and O. Bitchaeva, eds.) NATO AS Series, 2/34. Klitwer Academic Publisher, Dordrecht-Boston-London.

Gadd, G. M. (1988). "Accumulation of metals by microorganisms and algae." In: Biotechnology - A Comprehensive Treatise (H.J. Rehm, ed.). VCH Verlagsgesellschaft, Weinheim, pp. 401-433.

Mullen, M. D., Wolf, D. C., Ferris, F. C., Beveridge, T. J., Flemming, C. A., and Bailey, F. W. (1989). "Bacterial sorption of heavy metals." Appl. Environ. Microbiol. 55:3143-3149.

Murugaiyan, M. and Sivakumar, K. (2022). Optimization of process parameters for the removal of copper metal using brown alga *Padina gymnospora*. IJESRT. DOI: 10.29121/ijesrt.vii.i/2022.4.

Neilands, J. B. (1983). "Siderophores." In: Advances in Inorganic Biochemistry. Vol. 5. (L. Eichhorn and L.G. Marzilli, eds). Elsevier/North Holland, Amsterdam, pp. 137-166.

Poole, R. K. and Gadd, G. M. (1989). Metal-Microbe Interaction. IRL Press, Oxford.

Schmitt, D., Ller, A.M.E., Cso, Z., Frimmel, F.H. and Posten, C. (2001). The adsorption kinetics of metal ions on to different microalgae and *Siliceous* earth, Water Research, 35: 779-785.

Schneider, I.A.H., Rubio, J. and Smith, R.W. (2001). Biosorption of metals onto plant biomass: Exchange adsorption or surface precipitation, Int. J. Mineral Processing, 62: 111-120.

Sivakumar, K. and Anbazhagan, C. (2004). *Sargassam wightii* as a biosorbant for coper metal, Geo Bios 31(4): 299-301

Volesky, B. (1990). Biosorption of Heavy Metals. CRC Press, Boca Raton-Ann Arbor-Boston.

Volesky, B. (1992). Advances in biosorption of metals: Selection of biomass types. FEMS Microbiol. Rev. 14: 291-302.

Whitton, B.A. and Say, P.J. (1975). Heavy metlas, in River Ecology. B.A. Whitton (Ed.), Blackwell Scientific Publ., pp.286-311.