COMMENTARY

Bioremediation of Toxic Metals and Metalloids for Cleaning Up from Soils and Sediments

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Abstract: Pollution of soils and sediments by metals and metalloids is a serious environmental problem and threat to the ecological health and environmental quality. Microorganisms are known capable of detoxifying metals and metaloids into insoluble or non-bioavailable forms so that bioaccumualtion can be prevented under selective conditions. A key issue involved in bioremediation is the very poor understanding on the chemistry of the pollutants, specifically the bioavailable concentartions of metals and metalloids in the environmental matrices, especially soils and sediments and at the relevant pH value. Chemical states of the pollutants in terms of speciation are crucial to the possible success of any remediation practice, but it is impossible to conduct an effective operation for cleaning up without such information in mind. In the literature available, it is a common trend and practice to justify bioremediation for in situ application by using pure cultures of microorganisms, but this is a very prematured and bold attempt to applying microorganisms for in situ cleaning up without any scientific ground to support. For polluted soils and sediments, microorganisms have no role for cleaning up but phytoremediation is an effective means to remove and extract toxic metals and metallods from the complex soil matrices. This has been demonstrated successfully with a number of metals and organics as well as organic pollutants in both laboratory and also field trials.
Keywords: bioremediation; chromium; metals; metalloids; transport; uptake; assimilation; phytoremediation; clean up

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Received: November 1, 2018; **Accepted:** November 23, 2018; **Published Online:** November 25, 2018
Citation: Ji-Dong Gu, 2018. Bioremediation of Toxic Metals and Metalloids for Cleaning Up from Soils and Sediments. http://doi.org/10.26789/AEB.2018.02.006.

1 Introduction

Metals and metalloids are known environmental pollutants in air, water, and sediments and soils. They are natural consitituents of rocks and minerals (Dixon and Weed, 1977), and cen be released at high concentrations as a result of the intensive processing and anthropogenic activities, including mining, refinery and manufacturing. Chromium (Cr), Lead (Pb), Mercury (Hg) Cadmium (Cd) and Arsenic (As) are some of the selective ones with serious environmental consequences at high concentrations in environments and ecosystems. Because they are commonly used in industrial manafcturing processes, their discharge into the environment is often detected at elevated concentration. They are known to be toxic and have been reported widely, and, as a result, environmental regulations are now in place to regulate and control their discharge to protect humans and also the ecosystem health (Cheung and Gu, 2003).

Metals and metalloids are very complex in their chemistry, and their toxicity is a function of their bioavailable concentartion, not the total concentration, to the receptive organisms. They occur in a number of chemical states and forms in natural environment and have a range of bioavailability depending on the environmental martices, the ambient pH conditions and also chemical ligands. For example, Cr^{6+} is widely applied in industries, including electroplating, wood preservation, leather-tanning and alloy production for its strong anti-corrosion properties (Kimbrough et al., 1999; Khan, 2001; Dixit et al., 2002), but the high solubility of Cr^{6+} makes it highly mobility and bioavailability, and therefore posing extensive hazards to humans and ecosystems even at low concentration. At physiological relevant pH value, many of these metals and metalloids are not in their ionic soluble checial forms or state, but precipiated in various forms as minerals or hydroxides or hydroxyoxides. This simple fact has not been appreciated by many environmental toxicologitsts or biologists and, because of this, a large number of the toxicity data can be misleading and incorrect because the chemical concentration is nenver checked or confirmed in their testing. Detoxification of toxic metals can be achieved by conventional physicochemical processes abiotically (Xu et al., 2005a, b) and also biologically by microorganisms (Cheung and Gu, 2003) and plants (Yu and Gu, 2006, 2007a, b; Yu et al. 2006, 2007, 2016).

2 Chemical Speciation

Most of the toxic forms of elements are ionic metals and metalloids in their cationic or anionic form or elemental form. Ionic forms of them are very sensitive to pH conditions, especially the availability of OH^- and further interactions with clay minerals can form hydroxyoxides and oxides (Dixon and Weed, 1977). They can also react with humic substances to form sorbed or complexed organic- or inorganic-metals, resulting in a decrease of the inoic concentration, and reactivity and availability to biota. An effective and meaningful assessment of metals and metalloids in ecosystem then must be based on bioavailable concentrations of them, not the total concentration determined analytically to be realistic and meaningful. For inorganic toxicants, one technical approach to distinguish the different chemical forms is by means of chemical fractionation procedures widely used so that the same chemical of interest is determined according to their chemical binding forms in the samples. One of the most commonly adopted method is the procedures proposed by Tessie et al. (1979), in which the concerned metals or metalloids are chemically extracted based on their chemical states in the matrices of the sample environment, water and/or sediment by different chemicals. Such procedure allows the quantitative determination of the concentration of a selective toxicants from various fractions of the matrices, namely free ion, exchangeable form, carbonate bound, Fe and Mn oxides bound, organic bound, and residual (mineral structural lattice). This procedure, though debated from time to time, offers an operational procedure with high reproducibility to generate data with relevance to the toxicity of the chemical to the target organisms in the environment. Most importantly, it is biologically meaningful (Lai et al., 2005). Generally, the combined water soluble and carbonate bound can be taken as the bioavailable fraction for toxicity assessment in practice.

Metals and metalloids in environmental samples are strongly affected by the ambient pH condition: an increase of pH value can significantly lower the concentration of a specific metals or metalloids (cationic form) to very low concentration. This is a practice frequently employed in wastewater treatment and emergence response to accidental spill of metals and metalloids to aquatic ecosystems. An observed decrease of a metal concentration in the aquesous phase does not correspond to their removal or elemination from the specific environmental compartment, actually metals are often transformed between soluble and insoluble states, but the total concentration stay virtually unchanged for majority of them with only a few exceptions (Stumm and Morgan, 1996). Metal, Hg as an example, can form organo-metal complexes, methylated Hg of CH_4-Hg^+ and CH_4-Hg-CH_4, and such organic complexes can be volatilized into the atmosphere, resulting in relocation and transportation of the pollutant from initial ecosystem to a different site over physical distance. In addition, uptake of methylated metals generally increases by organisms to result in toxicity.

3 Bioremediation

Bioremediation is the active participaton and involvement of microrganisms or plant in the destruction or removal of the pollutants from a selective environment so that the toxicity of the toxicant concerned can be decreased to a non-detectable level. Many plants and photosynthetic organisms including cyanbacteria and algae can assimilate, accumulate and transform selective pollutants to some extent (McIntyre, 2003; Kuffner et al., 2008). Microorganisms can achieve the goal through their biochemical metabolism to destruct the organic pollutants and detoxify or precipitate the inorganic ones (Gu, 2016). Selective microorganisms are also capable of detoxification of soluble and toxic Cr^{6+} to insoluble and non-toxic Cr^{3+} [commonly as $Cr(OH)_3$] enzymatically under either sulfate-reducing (anaerobic) or aerobic conditions by the relevant microorganisms involved (Cheung and Gu, 2003, 2007; Ryan et al., 2002). At the same time, biological reduction of Cr^{6+} can also be achieved indirectly with reactive metabolites, such as ascorbic acid (Xu et al., 2005a, b) and H_2S produced by sulfate-reducing microorganisms (Cheung and Gu, 2003), or through direct enzymatic reactions (Cheung and Gu, 2003, 2007). In addition, microorganisms also have biochemical capability of methylating Hg and As to enable them to be volatile into atmpsphere for mobility and transport from the local goecompartment into another and also transportation over long distance (Han and Gu, 2010). Such biochemical reactions on metals and metalloids can result in significant reduction of both the total concentartiona and also the biologically active fraction of the specific metals or metalloids in sediments and soils.

It should aso be pointed out that microbial remediation generally suffers from inability to remove the metal species from the environment to significantly lower the active (toxic) fraction of the concentration, especially when dealing with sediment and soil to achieve a cleaning up. With water withiut sludge, application of microbial process can be effective beause the biomass can be concentrated and separate from the water so that the water is clean. This fact limits the application of microbial driven remediation in complex environmental matrices of soil, sediment and sludge, but far too many publications agnore this simple fact and blindly claim for bioremediation in soil and sediment.

Phytoremediation as an effective biotechnology to tackle the contamination of metals and metalloids has a unique niche for environmental applications. Green technology for environmental remediation has its own competitive role in relocation of the soluble and bioavailable fraction of the toxic metals and metalloids from solution phase or adsorbed phase into the green plants for accumulation and possibly detoxification and stabilization (Yu and Gu, 2007a, b; 2008a, b). This initial step of assimilation and then accumulation into plant biomass allow the concentration of pollutants into the plant biomass from soils or sediments to separate them from the initial contaminated environment. This capability of plants has been shown for toxic metals and metalloids, and many different plant species are available for application in cleaning up of the contaminated sites (McCutcheon and Schnoor, 2003). Among the different plant species, willow, hybride wilow and poplar has shown ability in assimilation of not only Cr (VI) and Cr (III) (Quaggiotti et al., 2007; Yu and Gu, 2007a; Yu et al., 2007), and selenate and selenite (Yu et al., 2007), but also iron cyanide complexes and methyl *tert*-butyl ether (MTBE) (Yu and Gu, 2006; Yu et al., 2006). Accumulation of Cr (VI) in hydroponically grown hybrid willow (*Salix matsudana* Koidz × *alba* L.) results in accumulation mostly in the roots reaching an approximately 50% and very little found in shoots and leaves (Yu et al., 2007). Since very little is transported and accumulated in leaves, this makes utilization of plants a promising and feasible means because annual fell of leaves will not contribute to a contamination issue for environmental and health concerns. Similar results are also observed for Cr (III) with removal of more than 90% from the solution (Yu and Gu, 2007a). Willow is very easy to generate seedlings from a mature tree readily through cutting from the mature tree and propogate under natural condition to develop into single seedlings with new roots and leaves. The seedlings can then be used for planting.

Green plants, willow and poplar, can be promoted for their growth and also for effectiveness in removal of pollutants from soils and sediments by fertilization and other means. Synthetic chelating agent ethylenediaiminetetraacetic acid (EDTA) and external application of nitrogen fertilizer can enhance the uptake and accumulation of Cr (VI) and Cr (III) into willows because the plant growth is enhanced (Yu and Gu, 2008a, b). This information yields another dimension for the bioremediation technology for manipulation when pants are used.

4 Conclusions

Bioremediation as a technology requires a good command on the chemsitry of the pollutants, especially the effective concentation. Successful execution of any cleaning up depends on the specificity of the site characteristics and either microorganisms or plants can be selectied and used effectively to achieve a cleaning up of pollutants from the sediment and soil effectively. It is very important to understand and appreciate the fact that microbial detoxification in the testtube is far from application so that remediation means can be chosen effectively with a scientific basis.

Acknowledgements

The research work discussed here is supported in part by Hong Kong SAR Gonerment.

Conflict of Interest

Author declares that there is no conflict of interest in this research.

Ethical approval

This article does not contain any studies with human participants or animals performed by the author involved.

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