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Arsenic Attenuation through Phytochemistry

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Abstract

Inorganic pollutants, which when present in higher concentrations than the permissible or prescribed limits, contaminate both soil and aquatic bodies and affect human health and environment very badly. Focusing on the damages caused by inorganic forms of Arsenic (As) chemicals to health and environment, the paper presents an overview of the investigation of As remediation through photochemistry.

Keywords: Phyto-remediation, Arsenic, Lead, Chromium, and Mercury (Hg).

Introduction

Arsenic (As) contamination of ground water is one of the most hazardous forms of ground water pollution which often happens due to naturally occurring high concentrations of arsenic in deeper levels of ground water. It is a high-profile problem which happens due to the use of deep tube wells / bore wells for water supply particularly in the Gangetic Delta, causing serious arsenic poisoning to large scale population inhabiting the area. About 150 million people around the world are estimated to be globally affected with As poisoning and new areas are continually being discovered. Arsenic contamination of ground water is found in many countries throughout the world, including the USA. Approximately 20 major incidents of groundwater arsenic contamination have been reported, out of which four major incidents

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occurred in Asia, in Thailand, Taiwan, and Mainland China. Arsenic, a well-known carcinogen, is considered as one of the world's most hazardous chemicals.

Contamination of air, water and soil is a major environmental concern, due to dispersal of industrial and urban wastes generated by human activities, Controlled and uncontrolled disposal of waste, accidental and process spillage, mining and smelting of metalliferousores, sewage, sludge application of agrochemicals to agricultural soils are responsible for the migration of contaminants into non-contaminated sites as dust or leachate and contribute towards contamination of our ecosystem. Although most of the metals are essential, all metals are toxic beyond certain concentrations, because they cause oxidative stress by formation of free radicals. Another reason why metals are toxic is that they can replace essential metals in pigments or enzymes disrupting their function. Thus, metals over and above certain permitted concentrations render the land unsuitable and unfit for plant growth and destroy the biodiversity.Due to its high toxicity, arsenic is seldom used in the western world, although in Asia it is still a prevalent and popular pesticide. Arsenic is mainly encountered occupationally in the smelting of zinc and copper ores. Belatedly, the studies have been carried out to remove these contaminants safely and economically with the help of plants and their species (phytoremediation) particularly those of Pterisvitatta (Chinese brake fern), Pteriscretica and members of poacea family whereby plants and grasses interact with the metals specifically. Phytoremediation refers to the treatment of environmental problems through the use of plants that mitigate the environmental problems without excavating the contaminants and disposing them elsewhere. It is, in fact, restoring balance through bioremediation.Belatedly it has emerged one of the fast emerging disciplines of bioremediation, where a lot of field applications were initiated throughout the globe in which inorganic, organic, nuclear (radionuclides) and other toxic wastes are being treated through. Toxic heavy metals and organic pollutants are the major targets of removal through the use of plant kingdom.This sustainable and inexpensive process is gathering importance as an alternative to conventional methods of remediation and, therefore, will be most suitable for a developing country like India. It involves the direct use of green plants and the micro organisms associated with it to stabilize or to reduce contaminants in soils, sediments, sludges, surface and ground waters. Heavy metals such as Arsenic (As), Lead (Pb), Chromium (Cr) and Mercury (Hg) etc., are potential environmental contaminants which cause health hazards not only to flora and fauna but also to human beings as well. Off late, the studies have been carried out to remove these contaminants safely and economically with the help of plants.

Arsenic contamination of soil and ground water is increasing day by day in India and other parts of the world due to host of reasons. In India, Bengal and certain parts of Jharkhand are worst affected by this menace whereas Rajnandgaon district in Chhattisgarh and Patancheru Industrial area of Hyderabad are no exceptions to this malaise. The possible cause of arsenic contamination in Bengal is the geochemical reactions such as oxidation of arsenic rich pyrites during the extraction of water via extraction process. The As content in ground water in Bengal Basin varies from 0.05 to 3.7 mg/L with an average of 0.2 mg/L which is much higher than the prescribed limit of 0.010 mg/L recommended by WHO in drinking water. It is mainly due to accumulation of heavy metals in soils as a result of chemical and industrial effluents absorption mainly from paper mills, fertilizers, glasses and mining wastes. The presence of heavy metals in toxic concentrations can result in the formation of superoxide radicals (O^{2-}), hydrogen peroxide (H_2O_2), hydroxyl radicals (OH^-), etc., which can cause severe oxidative damage to biomolecules like lipids, proteins and nucleic acids. Cr, Cu and Zn can induce the activity of various antioxidant enzymes and also non-enzymes like ascorbate and glutathione.Though several regulatory steps have been implemented to reduce or restrict the release of pollutants in the soil, they are not sufficient enough for checking the soil contamination. Metalcontaminated soil can be remediated through physical, chemical and biological techniques.

Remediation Techniques

Arsenic in groundwater exists primarily as oxy anions in two oxidation states: As (III) (as arsenite) and As (V) (as arsenate), both within the pH range of 6–9.Removal of As mainly depends on the composition and chemistry of the As in contaminated water. Arsenic occurs as As (III) in most of the reported cases and oxidation of As (III) to As (V) is considered necessary for the removal of As from the contaminated source. The main purpose of oxidation is to convert soluble As (III) to As (V), which is then followed by precipitation of As (V). This is essential for anoxic ground water, since As (III) is the prevailing form at near neutral pH. As (V) adsorbs more freely on to solid surfaces than As (III) and, therefore, oxidation followed by adsorption seems to be effective method for the removal of As. In fact, a wide range of technologies has been developed for the As removal from the drinking water over the years which may include coagulation, precipitation, adsorption, ion exchange, and membrane techniques. But other remediation techniques are also available which may include removal through phytochemistry and through the use of bacteria whereby As is removed by catalyzing biological processes.

The conventional ex-situ methods applied for remediating the polluted soils relies on excavation, detoxification and/or destruction of contaminant physically or chemically on or off the site. Consequently the contaminant undergoes stabilisation through solidification, immobilisation, incineration or destruction.Effective in January 2006, the US Environmental Protection Agency (EPA) reduced the maximum contaminant level (MCL) for arsenic in drinking water to 10 parts per billion (ppb).

In-situ method remediation, however, is done without excavation of the contaminated site. Reed et al. defined in-situremediation technologies as destruction or transformation of the contaminant, immobilisation to reduce bioavailability and separation of the contaminant from the bulk soil. In-situ techniques are favoured over the ex-situ techniques due to their low cost and reduced impact on the ecosystem. Conventionally, the ex-situ technique is to excavate soil contaminated with heavy metal and their burial in landfill site. But the offsite burial is not an appropriate option because it merely shifts the contamination problem elsewhere and also because of the hazards associated with the transportation of contaminated soil. Diluting the heavy metal content to safe level by importing the clean soil and mixing with the contaminated soil can be an alternative of on-site management. Immobilization of inorganic contaminant can be used as a remedial method for heavy metal contaminated soils which can be achieved by complexing the contaminants, or through increasing the pH of the soil by liming. Increased pH decreases the solubility of heavy metals like Cd, Cu, Ni and Zn in soil. Most of these conventional remediation methods are costly to implement and cause further disturbance to the already damaged environment.

Belatedly phytoremediation or plant-based bioremediation has emerged one of the promising tools of removing soil and water contamination from the environment. It uses green plants and their associated micro biota for the in-situ treatment of contaminated soil and ground water. The idea of using metal accumulating plants to remove heavy metals and other compounds was first introduced in 1983, but the concept has actually been implemented for the past 300 years. This technology can be applied to both organic and inorganic pollutants present in soil (solid substrate), water (liquid substrate) and the air. The physico-chemical techniques for soil remediation render the land useless for plant growth as they remove all biological activities, including useful microbe such as nitrogen fixing bacteria, mycorrhiza, fungi, as well as fauna in the process of decontamination. The conventional methods of remediation is very costly and may entail \$10to 1000\$ per cubic meter, however, remediation through phyto extraction may cost as low as \$ 0.05per cubic meter. The present paper deals with Arsenic attenuation or removal through phytochemistry especially through phytoextraction of heavy metal-contaminated soil using in-situ technique. Arsenic attenuation or removal through phytochemistry or through phytoremediation consists of five main processes enumerated below:

Rhizofiltration

It is defined as the use of plants, both terrestrial and aquatic; to absorb, concentrate, and precipitate contaminants from polluted aqueous sources with low contaminant concentration in their roots. Rhizofiltration can partially treat industrial discharge, agricultural runoff, or acid mine drainage. It can be used for lead, cadmium, copper, nickel, zinc and chromium, which are primarily retained within the roots. Plants like sunflower, Indian mustard, tobacco, rye, spinach and corn have been studied for their ability to remove lead from effluent, with sunflower having the greatest ability. Indian mustard has proven to be highly effective in removing a wide concentration range of Pb (4-500mg/l). The technology has been tested in the field with uranium (U) contaminated water at concentrations of 21-874 ug/l,the treated U concentration reported by Dushenkov was < 20 ug/l before discharge into the environment.

Phytostabilisation

It is mostly used for the remediation of soil, sediment and sludges and depends on roots ability to limit contaminant mobility and bioavailability in the soil. Phytostabilisation can occur through the sorption, precipitation, complexation, or metalvalence reduction. The plants' primary purpose is to decrease the amount of water percolating through the soil matrix, which may result in the formation of hazardous leachate and prevent soil erosion and distribution of the toxic metal to other areas. A dense root system stabilizes the soil and prevents erosion. It is very effective when rapid immobilisation is needed to preserve ground and surface water and disposal of biomass is not required. However, the major drawback of this process is that, the contaminant remains in soil as it is, and therefore requires regular monitoring.

Phytoextraction

Also referred to as phytoaccumulation, it is by far the best approach to remove the contamination primarily from soil and isolate it, without destroying the soil structure and fertility. As the plant absorb, concentrate and precipitate toxic metals and radionuclide from contaminated soils into the biomass, it is best suited for the remediation of diffusely polluted areas, where pollutants occur only at relatively low concentration and superficially.

Phytovolatilization

Phytovolatilization involves the use of plants to take up contaminants from the soil, transforming them into volatile form and transpiring them into the atmosphere. Phytovolatilization occurs as growing trees and other plants take up water and the organic and inorganic contaminants. Some of these contaminants can pass through the plants to the leaves and volatilise into the atmosphere at comparatively low concentrations. Phytovolatilization has been primarily used for the removal of mercury, the mercuric ion is transformed into less toxic elemental mercury. The disadvantage that the mercury released into the atmosphere is likely to be recycled by precipitation and then redeposit back into ecosystem. As per Dushenkov, phytovolatilization has been successful in removal of tritium (^3H), a radioactive isotope of hydrogen, which decays to stable helium with a half-life of about 12 years.

Phytodegradation

In phytoremediation of organic compounds, plant metabolism contributes to the contaminant reduction by transformation, degradation, stabilisation or volatilising contaminant compounds from soil and groundwater. Phytodegradation is the breakdown of organics taken up by the plant to simpler molecules that are incorporated into the plant tissues. Plants contain enzymes that can breakdown and convert ammunition wastes, chlorinated solvents such as trichloroethylene and other herbicides. The enzymes are usually dehalogenases, oxygenases and reductases. Rhizodegradation is the break down of organics in the soil through microbial activity of the root zone (rhizosphere) and is a much slower process than phytodegradation. Yeast, fungi, bacteria and other micro-organisms consume and digest organic substances like fuels and solvents.

Mechanism or metabolicfate of As during remediation

Arsenic which is predominantly available as Arsenate, As(V) in the soil is reduced to Arsenite, As(III) with the help of Arsenate reductase present in the plant species. Having reduced to As(III), it is able to form complexes with the help of electron donor proteins and gets detoxified. This complex so formed is translocated into the plant and is stored in the vacuole of roots and leaves of the plants. Finally, the plants can be harvested and the arsenic complexes extracted from it may be recycled to get metal back.

Future of As attenuation through phytochemistry

One of the key aspects to the acceptance of phytoextraction pertains to the measurement of its performance, ultimate utilization of by-products and its overall economic viability. To date, commercial phytoextraction has been constrained by the expectation that site remediation should be achieved in a time comparable to other clean-up technologies. So far, most of the phytoremediation experiments have taken place in the lab scale, where plants grown in hydroponic setting are fed heavy metal diets. While these results are promising, scientists are ready to admit that solution culture is quite different from that of soil. In real soil, many metals are tied up in insoluble forms, and they are less available and that is the biggest problem. The future of phytoremediation is still in the developmental phase, and there are many technical barriers which need to be addressed before using it on a mass scale. Optimisation of the process, proper understanding of plant physiology and its heavy metal uptake and proper disposal of biomass produced still needs to be properly investigated.

Conclusion

Phytoremediation is fast emerging as a cheap, sustainable, eco-friendly viable alternative to conventional methods of remediation, and will be most suitable for a developing country like India. Most of the studies have been reported from developed countries and knowledge of suitable plants is particularly limited so far as India is concerned. In India, commercial application of phytoremediation of heavy metals or organic compounds from the soil is in its rudimentary stage. Fast growing plants with high biomass and good metal uptake ability are needed. In most of the contaminated sites, hard, tolerant, weed species exist and phytoremediation through these and other non-edible species can restrict the contaminants from being introduced into the food web. Before thinking about disposal of contaminants, a better understanding of the involved potential mechanisms is of vital importance.

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