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EFFECT OF ORGANICS ON PHYTOREMEDIATION OF HEAVY METAL CONTAMINATED SOIL

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Abstract: *Organic amendments have been particularly beneficial to plant growth and microbial productivity when applied to acidic and nutrient-poor soils. Contaminated soils are difficult to establish plant growth on due to toxicity issues, but also due to unfertile, acidic or saline conditions. Established landfill sites and mine sites are perhaps the best examples. Organic amendments supply micronutrients particularly biosolids and MSW, and often possess moderate to high pH buffering capacity. Unlike organic contaminants, most metal do not undergo microbial or chemical degradation and two approaches are employed in mitigating their impacts and remediation of contaminated environments. These include (i) immobilization and (ii) mobilization of metal, thereby controlling their bioavailability. Bioavailability of metal plays a key role in both these two approaches .The bioavailability of metals in the soil environment has been defined as the fraction of the total metal in the interstitial pore water (soil solution) and soil particles that is available to the receptor organism. Recent studies have indicated that the transformation of contaminants in soils is a dynamic process which means bioavailability changes with time. A number of studies have documented the effect of ageing on the immobilization of metals in soils and also the potential value of various organic and inorganic soil amendments in reducing the bioavailability of metal in soil. The primary objective of this technique is to reduce the risk of metal reaching the food chain through plant uptake and off site contamination through leaching and erosion. Increasingly, plants with the associated microbial community are used to achieve the stabilization of metal contaminated soils (i.e. phytostabilization) .In the case of mobilization, the bioavailability of metal is increased by transforming the metal from the solid phase to the soil solution phase. A number of studies have demonstrated the value of various soil amendments such as EDTA in enhancing the mobilization of metal in soils.*

Keywords: *Phytoremediation, Heavy metal contaminated, Organics.*

Introduction: The term heavy metal includes elements with an atomic density of greater than 6g/ cm. Bioavailability can be minimized through chemical and biological immobilization of metals using a range of inorganic compounds, such as lime and phosphate compounds eg: appatite rocks and organic compounds. Bioremediation is a natural process which relies on bacteria ,fungi, and higher plants to alter contaminants and environmental conditions as these organisms carry out their normal life functions and can be enhanced by adding organic amendments to soil (ie., biostimulation /bioaugmentation).bioremediation of metal contaminated soils include technologies that involve biological agents including higher plants ,microorganisms and organic contaminants .This review focus on the potential value of organic amendments in the remediation of metalloids contaminated sites

Sources of Heavy Metals in Soil Environment: Heavy metals reach the soil environment through both pedogenic (or geogenic) and anthropogenic processes. Most metal occur naturally in soil parent materials, chiefly informs that are not available for plant uptake. Because of their low solubility, the metals present in the parent materials are often not available for plant uptake and cause minimum impact to soil organisms. Often the concentrations of metals released into the soil system by the natural pedogenic (or weathering) processes are largely related to the origin and nature of the parent material. Fertilizer, manure and organic amendments addition to agricultural soils is considered to be the major source of most minor elements including metals that are essential for plant growth.

Phosphate fertilizers are considered to be the major source of heavy metal input. There have been greater efforts to reduce the accumulation of Cd in soils through the use of low Cd-containing P fertilizers. This is achieved by either selective use of phosphate rocks (PR)s with low Cd or treating the PRs during processing to remove Cd. [1]. Organic amendments such as biosolid (e.g., Cd) and poultry manure (e.g., As) have been regarded as the major sources of metal accumulation in soils.. The heavy metals in biosolid most commonly of concern, Pb, Ni, Cd, Cr, Cu and Zn originate primarily from the contamination of these wastes with industrial waste water [2]. It was reported that the addition of biosolid enriched in Cu, Pb and Zn reduced the microbial biomasses C and N, indicating that the microbial activities were disrupted by the heavy metals[3]. Manure addition is increasingly being recognized as a major source of metal input to soils, with repeated applications having resulted in elevated concentrations of metals in soil. This can be major input of Cu to agricultural land estimated that 183 kg and 266 kg Cu and Zn, respectively, were added to soil through 8 years of swine manure application, most of which accumulated in the surface soil [4]. Similarly, regular use of growth promoters containing metals is likely to result in elevated concentrations of these metals in manure by products [5].

Reactions of Heavy Metals in Soils

1. Adsorption and Complexation: Sposito [6] defined sorption as the accumulation of a solute at the interface between the aqueous solution phase and solid phase. Adsorption indicates formation of surface complexes which can be either physical attachment or bonding of metal ions and molecules onto the surface of another component. Adsorption of charged solutes by a charged adsorbent can be classified into specific and non-specific retention [1]. In general terms, non-specific adsorption is a process in which the charge on the solutes balances the charge on the sorbent through electrostatic attraction, displacing other like-charged ions from the surface [7]. Specific adsorption refers to chemical bond formation between the solute and the functional groups on the adsorbent [8]. Adsorption of heavy metals strongly depends on soil pH [9]. For example, the amount of Pb sorption is a function of pH and increases sharply with pH, up to pH 5 and reaches a maximum at pH 8.0 with slight increase between pH 6 and 8; however, this depends on the adsorbent. The increase in Pb sorption with pH is attributed to an increase in negative charge, precipitation as hydroxides and formation of hydroxyl species that are more strongly retained compared to free metal ion species [10].Adsorption of heavy metals is also highly dependent on soil components that include silicate clays, organic matter, and iron, aluminium and manganese oxides [11]. Redox potential and cation/anion exchange capacity also control heavy metals sorption, but a single factor rarely accounts for their sorption in soil [12]. Metals form both inorganic and organic complexes with a range of soil components [1]. Soil organic matter has a high affinity for metal cations due to the presence of ligands or functional groups [13].When soil pH increases, H+ dissociates from functional groups such as carboxyl, phenolic, hydroxyl, and carbonyl functional groups, thereby increasing the affinity for metal cations [1]. The general order of affinity of heavy metals on organic matter is as follows [14]:

Cu2+> Hg2+> Cd2+> Fe2+> Pb2+> Ni2+> Co2+ > Mn2+> Zn2+> As (V) > As (III)

Certain factors affect heavy metal-organic complexes and these variables are temperature, solution and soil pH, ionic strength, dominant cations and soil type [1]. Soil pH is the most significant factor influencing metals–soil chemistry. For example, when pH increases the surface functional group is negatively charged. Consequently, metal cations are almost completely removed from soil solution at high pH [15]. Soil type and components have an important effect on heavy metals complexation.

2. Precipitation: Precipitation is an important process of metal immobilization in the presence of anions such as sulphate, carbonate, hydroxide and phosphate when the soil pH and the metal concentration are high [16]. Co-precipitation as well as precipitation as salts contributes to the immobilization of heavy metals [17]. Co-precipitation of metals takes place especially in the presence of Fe and aluminium (Al) oxyhydroxides [18]. For example, Contin et al. [19] reported co-precipitation of *Cd*, Cu, Ni, Pb and Zn onto precipitated Fe (hydr) oxides. Hydroxide precipitation is the most common and effective method of treatment for heavy metals [20]. Liming often increases the precipitation of metals. For example, Lee et al. [21] used granulated lime and calcium carbonate as coagulants to remove heavy metals from contaminated water. They showed that the main removal mechanism of heavy metals in their experiments was precipitation. Sulfide precipitation is also considered as an effective process for the precipitation of highly toxic heavy metal s. Metal sulfides are the least soluble minerals under reducing conditions. The attractive feature of the sulfide precipitation is the efficiency for metal removal over a broad pH range due to low solubility of metal sulfides and fast reaction [22]. However, to maintain low metal solubility using sulfides requires the maintenance of reducing conditions and for most surface soils is not practical. Lead forms precipitates with carbonates, phosphates, and sulphates present in the soil [23]. Lead precipitation with carbonate is more common in calcareous soil than in non-calcareous soil [24]. Park et al. [25] demonstrated the formation of Pb precipitates such as carbonate (PbCO3), chloride (PbCl2) and hydroxide chloride [Pb (OH) Cl] with the reaction of Pb with Mg/Al layered double hydroxides in aqueous solution. Phosphate compounds are the most common amendment to precipitate heavy metals effectively in contaminated soils or water. The usual stability sequence of metal phosphates is Pb > Cu > Zn [26].

3. Oxidation /Reduction: Arsenic, Cr, Hg and Se are most commonly subjected to microbial oxidation/reduction reactions, whilst divalent metals such as Zn, Cd, Pb and Ni are not. The oxidation/reaction reactions are grouped into two categories, assimilatory and dissimilatory. In assimiliatory reaction, the metals substrate acts as a terminal electron acceptor, thereby promoting bacterial growth. In the dissimilatory reactions the metals substrate has no specific function in the physiology of the microorganisms, and occurs by fortuitous reductions coupled to microbial oxidations of simple organic acids and alcohols, H_2 or aromatic compounds [27]. Some anaerobic bacteria use Se (VI) as a terminal electron acceptor for their growth. Reduction of Se (VI) to Se (0) is an important process to precipitate Se from contaminated water. Bacteria also enzymatically reduce Cr (VI) to the less mobile and toxic Cr (III), and reduce Hg (II) to volatile Hg (0), which can be used as a remediation strategy [28]. Cr (III) is strongly retained onto soil particles and less toxic than Cr (VI), the reduction of Cr (VI) to Cr (III) can enhance the immobilization of Cr, thereby rendering it less bioavailable. Lie et al. [29] isolated bacteria from Cr-contaminated landfill and demonstrated that toxic Cr(VI) was reduced effectively into comparatively less toxic Cr(III) by Bacillus sp. Sun et al. [11] reported the photochemical reduction of Cr(VI) by organic acids with-OH in the presence of Fe(III) and indicated that the complex formation between Fe(III) and organic acid is a key step for the photocatalytic reduction of Cr(VI).

4. Methylation/ Demethylation: Methylation is considered to be the major process of volatilization of As, Hg and Se in soils and sediments, resulting in the release of toxic methyl gas [30]. Although methylation of metals occurs through both chemical and biological processes, biological methylation is considered to be the dominant process in soil and aquatic environments. Thayer and Brinckman [31] grouped biomethylation into transmethylation and fission. Transmethylation implies transfer of an intact methyl group from methyl donor to another compound. Fission refers to the transfer of amolecule such as formaldehyde or formic acid from a methyl source to another compound. Afterward the resulting group is reduced to a methyl group. The metabolic methylation of inorganic as is considered to be a process of detoxification in aquatic organisms [32]. Inorganic As is methylated in the organism by alternating reduction of As (V) to As(III) and addition of a methyl group from S-adenosylmethionine to form methylarsonic acid and dimethylarsinic acid which are less reactive with tissue constituents and are more readily excreted in urine than inorganic As [33]. Methylation and demethylation are important processes regulating the Hg cycle in the environment [34]. Microorganisms can methylate Hg in water and soils. Methylation of Hg in the environment occurs mainly by biological processes involving sulfate reducing bacteria [35] under anoxic conditions [36]. Pongratz and Heumann [37] reported that bacterial culture released trimethyl Pb and monomethyl Cd as well as dimethyl Hg. Abiotic methylation of Hg can occur by methylcobalamin, methyltin compounds and humic matter. Among these methyl donors, humic matter is the most promising environmental methylating agent [38]. The reaction between oxidized mercury and small organic molecules such as acetic acid is considered as a potential abiotic methylation process. Oxidized Hg bound to thiols in humic molecules can be abiotically methylated by humic substances [7]. Demethylation of methyl

Hg can occur by both reductive and oxidative pathways and result from either cellular detoxification or metabolic processes in microorganisms. End products of reductive demethylation are CH4 and either Hg(II) or Hg(0) [39].

Sources of Organic Amendments: Organic wastes have been utilized as beneficial soil amendments for centuries. Animal manures have in the past been widely used as a source of essential nutrients and other benefits to soils. The more recent concern about soil contamination has resulted in organic wastes been used as materials for remediation of contaminated sites. In addition, the increase in wastewater generation and intensification of livestock has resulted in large quantities of solid organic wastes from very widely different sources with variable composition [40]. Several industries generate significant quantities of organic waste, such as paper mill factories, olive mills, etc. [41]. Municipalities generate several types of organic waste which may be used as a soil amendment for land reclamation [42]. Municipalities generate two major sources of organic waste for soil amendment. The major organically based by-products include biosolids (often referred to as sewage sludge) and municipal solid wastes (MSW). Municipal solid waste is the general waste stream generated in local municipalities, including garden waste. Organic waste is largely separated from other materials (i.e. general waste, glass, aluminium, and non-recyclables) for re-use often after composting [43]. Disposal of organic wastes is a significant issue for virtually all governments, with the soil area available for disposal of organic wastes declining over the last few decades [44]. Municipal solid wastes are derived from disposal of the general waste stream that includes food scraps and yard trimmings as well as miscellaneous products which are separated from non-compostable materials [45]. Ever the less, MSW often contain significant levels of heavy metals due to incomplete separation of industrial waste streams.

Mechanisms for Enhanced Bioremediation of Heavy Metals by Organic Amendments

1. Immobilization: It has often been shown that the addition of organic amendments to soils increases the immobilization of metals through adsorption reactions. The organic amendment-induced retention of metals is attributed to an increase in surface charge [46] and the presence of metal binding compounds [47]. Organic amendments were effective for immobilization of Cu by increased formation of copper–organic matter complexes, and for Cr by reduction from Cr (VI) higher valency to Cr (III) and subsequent precipitation as chromic hydroxide [48].

2. Reduction: Most metals are subject to abiotic and biotic redox reactions, which influence biogeochemical behaviour. However, redox reactions in soils are most important for As, Cr; Hg and Se. Organic amendments play a pivotal role especially in the reduction of this metal s by providing a source of electron donor and carbon substrate for microorganisms. It has often been noticed that addition of organic amendments such as manures and crop residues enhances the reduction of Cr and Se [49].

3. Volatilization: The majority of metals cannot be volatilized from soil or waters. However, As, Hg and Se may be volatilized through reduction and methylation reactions. For example, bacterial reduction of Hg (II) is known to be transformed to gaseous Hg (0) and subsequently lost to the atmosphere [50]. Similarly, biological methylation is effective in forming volatile compounds of As such as alkylarsines, which could easily be lost to the atmosphere. Volatile derivatives of as include arsines, mono-, di-, trimethylarsine and arsenic oxides. Volatile As compounds are more mobile, bioavailable and often considered more toxic in comparison to pentavalent arsenic species, but volatile methylated arsenic oxides are less toxic than As (III) and can easily and rapidly be oxidized and demethylated in air [51]. Therefore, biovolatilization can offer an effective remediation technology for as contaminated soil or water.

4. Rhizosphere Modification: Organic amendments have been shown to affect the chemistry (e.g., pH, organic acids, soil solution composition) and biology (e.g., microbial community) of soil. Similarly, it is being increasingly recognized that the soil immediately surrounding plant roots (rhizosphere) is a modified microbiologial and chemical environment due to plant–soil–microbe interactions. The changes in soil chemistry due to soil amendment and plant growth can therefore influence the transformation, mobility and bioavailability of metals [52].

5. pH: Application of organic amendments such as biosolids and manures often decreases the pH of rhizosphere soils. The rhizosphere acidification can be attributed to a combination of mechanisms, including: (i) cation–anion exchange balance; (ii) organic acid release (e.g., citric, malaeic, lactic, oxalic, propanic, butyric acids); (iii) root exudation and respiration and (iv) redox coupled processes involving changes in the oxidation state of Fe, Mn and N and consuming or producing of H+ [53]. In the rhizosphere, the various origins of H+ released by roots in their immediate vicinity and the underlying physiological mechanisms involved are now well elucidated.

6. Organic Acids: Rhizodeposition' describes the introduction of C compounds and nutrients by plant roots. This generally includes water-soluble exudates, secretions, lysates, gases and mucilage. Organic compounds such as carbohydrates, carboxylic acids and amino acids in rhizodeposits attract microorganisms and therefore are most responsible for additional microbial growth within the rhizosphere [54]. In the rhizosphere, the exudation of C-compounds has been the major research focus for its major impact on soil microbiology and C biogeochemistry, particularly the role the rhizosphere may play in global C cycling. Exudation of organic compounds can influence the behaviour of trace and toxic metals]. Certain low molecular-weight compounds released from plant roots (amino acids, carboxylic acids, sugars, and simple and flavonoid-type phenolics) [55] may form stable complexes with metal cations in the soil solution matrix, and can directly modify metal availability in the rhizosphere. The role of carboxylates has been examined for their potential impact on the biogeochemistry of metals through aqueous complexation and ligand exchange processes. Amongst the range of carboxylates exuded in the rhizosphere, malate, citrate and oxalate are expected to have the most dramatic effect due to their ability for complexation of metals [56]. Organic exudates are released from the roots when the plant is under stress from mineral deficiency and toxicity. Iron deficiency has been known to induce root exudation of a range of organic compounds to improve Fe acquisition in soils.

Efficacy of Organic Amendments for Bioremediation: Land application of municipal and industrial by-products has been repeatedly shown to increase the vegetative productivity of soils in agricultural and land reclamation settings. Indeed, animal manures have for a very long time been known to improve soil physical, chemical and biological attributes. More recently, plant growth has been shown to be improved by a large diversity of organic wastes, including biosolids, MSW, pulp-mill by-products and in certain cases, industrial wastes. Organic amendments have been particularly beneficial to plant growth and microbial productivity when applied to acidic and nutrient-poor soils. For example, Stephen and Lin [57] reported compost material increased the yield of Chinese white cabbage (Brassica rapa L.) only in nutrient-poor soils of Hong- Kong, and not produtive soils. Similarly, Sloan and Basta [58] showed that use of alkaline stabilized biosolids increased soil pH of acidic soils, reducing Al toxicity in plants. Biosolids without alkali treatment however do not appear to be an efficient liming agent, particularly in extreme acid conditions found at mine sites and acid sulfate soils]. Contaminated soils are difficult to establish plant growth on due to toxicity issues, but also due to unfertile, acidic or saline conditions. Established landfill sites and mine sites are perhaps the best examples. Organic amendments have also been shown to enhance productivity on alkaline, saline and calcareous soils. Organic amendments supply micronutrients particularly biosolids and MSW, and often possess moderate to high pH buffering capacity.

Conclusions: Regular applications of organic amendments such as bios lid and manure compost to agricultural soils improves the physical, chemical and biological fertility of soil. However traditionally these organic waste products have been considered as a major source of metal input to agricultural soils. Within the introduction of advance wastewater treatment technologies and improvements in field utilization in animal and poultry industries. The metal content of these waste products continuously decrease. Hence organic amendments that are low in metals can effectively utilized to remediates soils contaminated with toxic metals. Application of organic amendments reduce bioavailiability of metals through adsorption and complexion reaction thereby reducing their transfer through plant uptake and leaching. These amendments enhance the reduction of metals such as Se and Hg thereby resulting in release of volatile compounds. Phytoremediation is presently an effective method in the role of rhizosphere and their associated microbial assemblages.

Future Research Areas to be Persuaded: Impact of organic amendments, especially in the form of nano-material on the chemodynamics of metalloids and there subsequent bioavailability. Effect of organic amendments on rhizosphere biochemistry in relation to mettaloids dynamics. Long term stability and biogeochemistry of mettaloids immobilized by organic amendments. Nature and extent of soil mineral-organic matter-microbe interactions as influenced by environmental and edaphic factors.

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