

Heavy Metal Pollution of Environment by Mine Tailings and the Potential Reclamation Techniques: A Review

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Abstract

Environmental pollution through heavy metal has alarmingly been increased due to industrial and economic development worldwide. Since the industrial revolution started throughout the world, mining activities are being developed, generating huge amount of metal-rich hazardous wastes like tailings and thereby posing potential threat to terrestrial and aquatic ecosystems. The small tailings particles can easily be spread out of the tailings ponds to the surrounding environment because of erosion driven by rain water and strong wind. Subsequently, heavy metals of tailings particles enter into the food chain in different ways and result in serious health issues in humans and animals. Therefore, ecological restoration of mine wastelands is of paramount concern. Different methods for the remediation of mine sites have been developed so far, most of which are expensive and difficult to implement. Countries having severe heavy metal pollution issues are spending huge money every year for the management purpose of these pollution sources and still scientists are doing research to establish eco-friendly, cost-effective, easily-applicable and sustainable remediation strategies for the metal-rich mine tailing sites. This review describes the way of heavy metal contamination of environment by mine tailings, negative effects of heavy metals, research development regarding remediation methods as well as suggests some ideas for the future research direction.

Keywords: Mine tailings, heavy metal contamination, sustainable remediation method, phytoremediation, amendments

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1. Introduction

In the last few decades, heavy metal (HM) contamination has alarmingly been raised due to industrial and economic development worldwide, posing potential threat to terrestrial and aquatic ecosystems (Kou *et al.* 2018; Murtaza *et al.* 2017). Heavy metal load is being escalated in the environment from different anthropogenic sources because of its' non-biodegradable nature (Li *et al.* 2018), thereby causing harm to plants and humans via food chain (Ogbomida *et al.* 2018). With the rapidly flourishing metal mining industries, mine tailings has been emerged as one of the vital sources of environmental pollution by HMs worldwide (Mugica-Alvarez *et al.* 2015; Chen *et al.* 2018). Mining industries compulsorily generate tailings as a by-product, which are composed of sand, water, fine-grained solid material and significant amount of HMs (Santibañez *et al.* 2012). Mine tailings are often characterized by low organic matter content, poor water holding capacity, sandy texture and high metal concentration and normally, are dumped into open area known as tailings pond without any treatment (Candeias *et al.* 2015).

More than 10 billion tons of mine tailings are discharged annually in the world (Adiansyah *et al.* 2015). In USA alone, more than 500,000 abandoned mine sites have been identified; 38,500 of which were belonged to the national forest-lands, these are found to be connected with the destruction of water resources and ecosystems for more than a decade (Salam *et al.* 2019). About 12,000 tailings ponds are present in different areas of China, occupying a large area of land (Yin *et al.* 2011). These metal-rich small tailing particles can easily contaminate surrounding soil and water bodies via wind dispersal, surface runoff and leaching, creating disturbance to ecosystem (Sánchez-López *et al.* 2015). It has been estimated that nearly 10% of China's agricultural lands are affected by metal contamination (Kou *et al.* 2018) and around 20 million hectares of farmland are being polluted by toxic metals annually (Cai *et al.* 2019). At high concentration, HMs often impair the growth of plant root, and cause leaf discoloration and reduced biomass production (Jadia & Fulekar 2009). Therefore, ecological restoration of mine wastelands is of great concern.

In this review, we discussed on the nature of mine tailings, potential effect on the environment as being a potential source of HM pollution and remediation strategies of such mine wastes, which would provide valuable information for the readers interested in this kind of research direction.

2. General characteristics of mine tailings

Owing to the higher concentration of potentially toxic elements, the trashes and wastes from the mining units are

considered due be environmentally hazardous (Tordoff *et al.* 2000). In recent years, the mining activities of different countries gained much concern, since a vast area of land is getting disturbed by mining every year. With no exception, the mines pose severe threat to environment by escalating high levels of toxic elements and minerals, which further may aggravate the problems with low pH, high electrical conductivity (EC), low in organic matter, low fertility and poor physical properties (Ye *et al.* 2000). Typically, the pH of mine tailings are around near-neutral, however, the values may be ranged from highly acidic to alkaline (1.6-8.6) according to different environment. In general, EC of the tailings used to be very high approximately >200 mS/m, this indicates the possible salinity issues. Organic carbon (OC) contents usually low in tailings ($< 1\text{g } 100\text{g}^{-1}$), however the higher OC if found may be attributed by the vegetations on the tailing dam. Similarly the total N and total P may ranges <700 mg kg^{-1} and 52 to 4400 mg kg^{-1} , respectively; albeit it may differs in different environments (Ye *et al.* 2002; Conesa *et al.* 2006; Ma *et al.* 2006).

The total concentration of metals at any particular tailing doesn't necessarily reflect the bioavailable and potentially mobile fractions (Fergusson 1990); rather it just aids in estimating the associated risk factor thereby emphasizing the attention needed on that site. For estimating the bioavailable metal fraction, the diethylenetriaminepentaacetic acid (DTPA) method is very much beneficent. The DTPA-extractable metal concentration in tailings were reported to be remarkably lesser than total metal concentrations (Ma *et al.* 2006).

On the basis of mining processing and design of tailing dam, the texture of tailings differs from coarse to fine. As a result of stratification that occurs frequently in the tailing pond, coarser particles will started to settle in the areas near the inlet to tailing dam whereas, the finer materials may settles nearer to the outlets (Hossner & Hons 1992); which necessitate the crusting and cracking once it is dry. In addition, the extreme high or low water retentions are common in the tailings according to their texture. When the dark colored tailings are subjected to solar radiation, their surface temperatures may raise resulting excessive evapotranspiration and seedling dehydrations. Another major issue of fine tailing particles is the dust particles, since it may drastically contaminate the environment by their easy dispersion through wind and water (Hossner & Hons 1992). The textures of different tailings range from silty-loam to sandy-loam and sandy, and the physico-chemical properties of the tailings are not suitable for plant growth and development (Ye *et al.* 2002).

3. Deleterious effects of heavy metals on human health and plants

In literature the HMs contamination and their deleterious consequences on ecosystem and several living organisms been widely addressed by many researchers (Manivasagaperumal *et al.* 2011; Schneider *et al.* 2016; Kim *et al.* 2016); for instance their effects on environment, flora, fauna and on human health are the prime research area in current era. In environment, especially in soil it lowers the soil enzymatic activities, affects mineralization and nutrient cycling, reduce the formation of humic substances and soil organic matter thus affecting normal decomposition and material cycling (Ma *et al.* 2015; Cao *et al.* 2016). It also causes the land degradation resulting obstruction of normal functioning as well as contaminates and reduce the quality of air, water and soil in closer proximities from HMs source point (Schneider *et al.* 2016).

It directly influences the pigmentation, biosynthesis, transpiration and battery of antioxidant systems, causes lipid peroxidation which retard the plant growth (Wang *et al.* 2014; Xian *et al.* 2015). Besides environmental influences, their integration into the higher animals via soil-crop-food chain digs the attention on HMs management (Cheng *et al.* 2016). When exposed at higher levels and being carcinogenic agent HMs can cause severe dysfunction in different organs and may ultimately be fatal in higher animals and human beings (Cao *et al.* 2016).

The specific detrimental impacts of some HMs (Zn, Pb, Cd, Cu Hg, Cr, As, Ni and Al) on human health, plants and environment are described below.

3.1. Lead (Pb)

Various human activities such as mining, accelerated production and burning of fossil fuels have resulted the escalation of lead and associated compounds in all the medium such as air, water and soil; also affecting plant, higher animals and human beings through food chain (Nagajyoti *et al.* 2010). Products such as lead based paints, batteries, cosmetics, bullets, toys, gasoline, plumbing pipes and also other industrial emissions may expose lead into the environment besides HM contaminated soil (Thürmer *et al.* 2002; Martin & Griswold 2009). The industries and automobiles in the urban areas contribute a higher amount of Pb emission (Walraven *et al.* 2014). Thus Pb is one of the ubiquitously dispersed in the environment and is reported to be one of the toxic elements that present abundantly in soil; this element is not having any biological functions, not needed by the living system unlike some important micronutrient metal elements such as zinc, copper and manganese. In plants, it causes severe malfunctioning by affects their morphological integrity, growth and photosynthetic processes (Shu *et al.* 2012); in higher levels it inhibits the seed germination, causes water and mineral nutrient imbalances, alter the enzyme activities and affects membrane permeability (Hassan *et al.* 2014).

Lead is vicious substance that causes physiological as well as neurological problems to human beings; it enter

into the system via food or water (Abdelhafez *et al.* 2014); provided the Pb was found to be very persistent in aqueous environment (Nagajyoti *et al.* 2010). The extent of exposures caused different malfunctions; acute exposure lead to hypertension, renal dysfunction, abdominal pain, sleeplessness, fatigue, hallucinations, arthritis, high blood pressure, muscle and joint pain (Odum 2000); whereas, the chronic exposure results in birth defects, psychosis, autism, allergies, weight loss, muscular weakness, kidney damage, brain damage, and may even cause death (Martin & Griswold, 2009; Abdelhafez *et al.* 2014).

3.2. Zinc (Zn)

At a higher concentration, Zn exerts several negative impacts on the living systems. (Lin *et al.* 2012). In plants, Zn impacts several metabolic processes since being an essential micronutrient (Cakmak and Marshner 1993). For instant, it involves in the synthesis of various enzymes and proteins, participates in cell division, regulates nucleic acid metabolism (Nadgorska-Socha *et al.* 2013). The concentration of Zn in the range of 150-300 $\mu\text{g g}^{-1}$ of soil is regarded to be toxic, especially to plants (Emamverdian *et al.* 2015), causing stunted growth, lowering biomass and reduction in crop yield (Soudek *et al.* 2014). At higher concentrations, it can generate excess ROS (reactive oxygen species) and deficiency of Fe and P, results in oxidative stress, chlorosis and necrosis, reduction in pigmentation and photosynthesis and ultimately causes membrane disruptions (Tsonev *et al.* 2012). It also alters the catalytic efficiency of enzyme systems in many plants like pea plants (Romero-Puertas *et al.* 2004). In humans, it causes malfunctioning of system resulting in hindrance of growth and reproduction; clinical signs includes vomiting, fatigue, dizziness, bloody urine, yellowing of mucus membranes, anemia, diarrhea and multiple organ failures ((Duruibe *et al.* 2007; Ali *et al.* 2013).

3.3. Cadmium (Cd)

Cd is a HM with the specific gravity of about 8.56 times higher than that of water. Cd released into the environment from geogenic origins such as volcanic eruption, weathering and river transport; some of the anthropogenic sources include mining, incineration of municipal wastes, extensive usage of fertilizers, tobacco smoking and as a byproduct during Zn manufacturing (Wahid *et al.* 2008). The regulatory limit of cadmium (Cd) in agricultural soil is 100 mg kg^{-1} soil (Salt *et al.* 1995).

Cd when compared to the other HMs (e.g. Pb, Cu), are highly bioavailable and soluble in soil solutions increasing their phytoavailability and highly leachable by groundwater respectively (Perronnet *et al.* 2000). Besides, Cd is often found in plant parts such as grains, vegetables and fruits due to their higher above ground translocation rates (soil to plant transfer) (Satarug *et al.* 2010). The plants grown in highly polluted soil shows the symptoms of visible leaf chlorosis, browning of leaf and root tips, leaf roll and damage in PS-I, PS-II photosystems, growth inhibition and further to necrosis and plant death (Guo *et al.* 2008; Daud *et al.* 2013). Being a highly toxic and non-essential HM, it causes adverse effects on plant enzymatic systems, initiates oxidative stress and also causes nutritional deficiency in the plant systems (Irfan *et al.* 2013).

The international agency for research and cancer classified cadmium and related compounds under Group I carcinogenic agents to human beings (Henson & Chedrese 2004). Inhalation and ingestion is the major exposure pathway to human beings; upon degree of exposure it may results in acute or chronic conditions (Chakraborty *et al.* 2013). Generally the Cd exposure causes vomiting, nausea, abdominal cramps and diarrhea, muscular weakness and dizziness followed by convulsions, shock and unconsciousness; whereas in higher concentrations, it causes pulmonary emphysema, skeletal damage (osteoporosis), kidney damage, lung cancer and prostate cancer (Li *et al.* 2014). In addition, the women exposed high during pregnancy results in premature birth and reduced birth weights (Henson & Chedrese 2004).

3.4. Copper (Cu)

Copper has been regarded as a salient pollutant of the air and agricultural soils; rigorous usage of fungicides, pesticides, herbicides, organic sludges and manure applications escalates the concentration of Cu in agricultural soils (Panou-Filotheou *et al.* 2001). Besides intensified industrialization, smelting and mining activities significantly increased the levels of Cu in ecosystems. Cu is the essential micronutrient for plant that plays impeccable role in cell wall metabolism, CO₂ assimilation and ATP synthesis (Goswami *et al.* 2016). An excessive amount of Cu in soil is cytotoxic to plants posing severe stress and engenders plant injury. Cu toxicity fosters a remarked reduction in plants' root volume obstructing water, mineral and nutrient uptake which may lead to chlorosis, necrosis and growth retardation (Singh *et al.* 2007). It also generates the excessive ROS that leads to oxidative stress which disturbs the metabolic pathway and damages to macromolecules (Goswami *et al.* 2016). In contrast, primarily the Cu is exposed to the human beings through the consumption of Cu-laden food and water. Excessive intake may results in mucosal irritation and corrosion, capillary damages, hypo-chromic anemia, osteoporosis, gastrointestinal irritation, hepatic and renal damage (USEPA 2002).

3.5. Mercury (Hg)

Mercury is highly toxic HM that released into the environment through various industrial activities such as pharmaceuticals, paper and pulp preservatives, agro-industry, coal and metallurgy, metal refineries, chlorine and caustic soda productions (Morais *et al.* 2012; Chen *et al.* 2012). In addition, Hg is extensively employed commercially for making fluorescent bulbs, thermometers, electronic switches and other products (Shanley *et al.* 2002). Hg has the capability of amalgamating with other elements and takes various organic and inorganic forms; out of which its organic form is predicted to be highly poisonous (Hosseini *et al.* 2013).

The ionic form of mercury (Hg^{2+}) mostly prevails in agricultural soil and can easily accumulate in different plants (Wang and Greger 2004; Israr *et al.* 2006). For instance, Hg^{2+} can readily bind to water channel proteins, thus exerts closure of leaf stomata resulting barrier in water flow within plant parts (Zhang and Tyerman 1999). At high levels, it also obstruct mitochondrial functioning, triggers ROS generation and oxidative stress that leads to disruption of membrane lipids as well as affects normal cellular metabolisms (Israr *et al.* 2006). In humans, the exposure to high levels of mercury can cause harm to the brain, kidneys and the developing fetus (Alina *et al.* 2012). Organic Hg exposure significantly contributed by consuming fishes and aquatic animals. The common symptoms of organic Hg poisoning are headache, memory problems, fatigue, tremors and hair loss (Ainza *et al.* 2010).

3.6. Chromium (Cr)

Chromium exists in different oxidation states, but the trivalent (Cr^{3+}) and hexavalent (Cr^{6+}) are the most toxic forms to animals, humans and plants (Monalisa & Kumar 2013). Many industries widely employed chromium in their productions and manufacturing; mainly electroplating, metallurgy, production of paints and pigments, wood preservation, tanning, pulp and paper production (Ghani 2011).

Environmental Protection Agency (EPA), International Agency for Research on Cancer (IARC) and World Health Organization (WHO) classified chromium, especially Cr (VI) as a human carcinogenic agent (Shaffer *et al.* 2001; Jeyasingh & Philip 2005; Huang 2009). Inorganic forms of mercury cause congenital malformation, spontaneous abortion and gastrointestinal disorders. Whereas organic forms like monomethyl and dimethyl mercury may cause acrodynia, stomatitis, gingivitis, neurological disorders, total damage to the brain (Duruibe *et al.* 2007).

In plants, Cr causes inhibition in growth, chlorosis, wilting of leaf tops, root injury as well as nutrient imbalances (Ghani 2011); in general, its toxicity induces alterations in the germination process affecting growth retardation in different plant parts (roots, stems and leaves). Consequently, it reduces the total dry matter production of plant thereby affecting total yield (Shanker *et al.* 2005). Moreover, Cr also interferes plants' physiological functioning such as photosynthesis, water retention and affects mineral nutrition. It is been documented that the Cr may alters the metabolism through its direct influence on enzymes or metabolites as well as generation of ROS (Adrees *et al.* 2015).

3.7. Arsenic (As)

Arsenic is released into the ecosystem mainly due to the anthropogenic activities such as mining and ore processing (Matschullat 2000). The As toxicity in plants lead to the reduction of seed germination, retardation of plant growth, associated reductions in height, leaf area, tiller and panicle, dry matter, leaf chlorosis, reduction in yield as well as wilting of plant (Chibuike *et al.* 2014).

The inorganic forms of arsenic (arsenite and arsenate) are very much hazardous to human health; are carcinogenic substances causing different types of cancers such as lungs, liver, bladder and skin (Abdelhafez *et al.* 2014). More than 30 countries round the globe documented the major cause for the arsenic poisoning as contaminated drinking water (Chowdhury *et al.* 2000). WHO specified the limits of arsenic level in ground water as $10 \mu\text{g L}^{-1}$; if any drinking water sources that are having 10–100 times higher than the specified value can be consider as a severe threat to human health (Hoque *et al.* 2011). Based on the exposure, the arsenic toxicity may be either acute or chronic; the chronic toxicity normally termed as arsenicosis (Mazumder 2008; Li *et al.* 2014).

3.8. Nickle (Ni)

The anthropogenic activities such as smelting, mining, burning of oil and coal, application of phosphate fertilizers and pesticides introduces the Ni^{2+} in environment (Gimeno-García *et al.* 1996). Elevated concentrations of Ni^{2+} in soil may directly results in alteration of various physiological functioning in plant grown on that area; toxicity symptoms includes chlorosis, necrosis, impairment of nutrient balance and disrupts the membrane integrity in different plant species (Rahman *et al.* 2005; Ma *et al.* 2009). Generally the plants suffering from Ni^{2+} toxicity is indicated by the reduced uptake of water (Gajewska *et al.* 2006). The Ni toxicity in higher animals and humans resulted in various deformities such as inhibition of spermatogenesis, amylase enzymes, insulin production and kidney functioning (Ali *et al.* 2013). The nickel carbonyl $\text{Ni}(\text{Co})_4$ is the most menacing forms of Ni; are generated during cigarette smoking which may lead to severe pulmonary fibrosis (respiration disorders) and renal

malfunctioning (Srivastava and Gupta 1996).

3.9. Aluminum (Al)

Al is escalated in the environment during their mining processes (Gupta *et al.* 2013). It is reported to be highly toxic in acidic environment especially below 5-5.5, since increased bioavailability of Al³⁺. The soil surface with the lowered pH due to Al³⁺ toxicity is of great concern as it directly impacts the crop production (Emamverdian *et al.* 2015). Its interaction with plasma membrane and apoplastic, symplastic targets may affect the normal physiological and cellular functioning of plants. The common effects are root growth inhibition, cellular modification in leaves, leaf discoloration and death of leaves, and leaf necrosis (Gupta *et al.* 2013).

Dermal contact, inhalation and ingestion are the major routes of Al exposure in human beings. The Al contaminated drinking water, food, beverages, and certain drugs took important part in introducing Al to the human body. Symptoms like mouth and skin ulcers, nausea, rashes in the body, vomiting and diarrhea are due to the Al toxicity in humans; the symptoms are however only lasts for a short period and are mild (Clayton 1989). Nevertheless, WHO hypothesized the risk factor of Alzheimer disease (AD) will be increased if humans are constantly exposing to Al (WHO 1997); since Al causes adverse effects on central nervous system, problems with memory and balancing as well as loss of motor coordination (Krewski *et al.* 2007).

Due to the above mentioned adverse effects of different HMs on plants and human health, it is imperative adopt a safe and economically efficient remediation technologies for the remediation of HM polluted sites. Plant based technology assisted by soil amendments are considered as a potentially safe, green and economical technology. This technology is termed as phytoremediation, which is environment friendly, solar driven, non-destructive, non-invasive, clean and aesthetically pleasant (Singh *et al.* 2012; Yildirim *et al.* 2017).

4. Remediation technologies of heavy metal contaminated mine sites

Industrialization and urbanization led to the increase in the mining activities in order to meet out the market demand; continuous production as well as the exploitation of natural resources left behind escalation of metal content in the environment. Continuous mining have resulted in the conversion of vast sum of land into useless unproductive and barren sites round the globe. The prime motive of remediation of these sites is to reduce the risk of toxic metal contamination to the adjacent environment. The remediation technologies are mainly categorized into physical remediation, chemical remediation and biological remediation (Wang *et al.* 2017); mainly these categorization done on the basis of (i) the nature of action that is applied on the metal immobilization or extraction; (ii) the location where the process is applied (in-situ or ex-situ); and (iii) technology type (Dermont *et al.* 2008).

Physical treatments include excavation, land-filling, soil replacement, washing or solidification and thermal desorption. Traditionally on-site management or excavation used to clean up the polluted site, but such approach will only shift the problem to the other places and also additionally results in secondary pollution due to the transportation and containment on other sites (Thakur *et al.* 2016). In order to partly reclaim the soil or to dilute the metal content, soil replacement technique is helpful (Zhang *et al.* 2004). Soil washing ensures the elimination of metal content but it is inevitable to avoid the pollutant rich residues as a byproduct, and moreover the soil may become unsuitable for establishing vegetation (Tangahu *et al.* 2011). On the basis of pollutants' volatile nature, the contaminated soil were subject the thermal treatments by microwave, steam and infrared radiations in order to let the pollutant volatile (e.g. Hg, As) is called thermal desorption; the pollutant thus removed are retrieved by carrier gas or creating vacuum pressure (Li *et al.* 2010). But this is not popular since it needs expensive devices and desorption time consumption which limits their application in soil metal remediation (Aresta *et al.* 2008).

Chemical remediation methods involve chemical leaching, Chemical fixation, Electrokinetic remediation, Vitrify technology etc. washing out the contaminants from the soil using various solutions such as fresh water, reagent, other fluids or also chemical gases are called chemical leaching (Tampouris *et al.* 2001; Ou-Yang *et al.* 2010). The HMs bound in the soil substrate is transferred to the liquid phase by ions exchange, precipitation, adsorption and chelation during the soil chemical washing, further can be recovered from leachate. The chemical fixation used to fix/immobilize the soil metal contaminant through the addition of reagent which makes them less soluble, immovable, low toxic substances and eventually decreases their mobility in water or other environmental media as well as translocation to plants (Zhou *et al.* 2004). Whereas, in electrokinetic remediation, particular voltage is applied at the two ends of soil in order to form electric gradient, so that the pollutants will be carried towards two pole via electrophoresis, electric osmosis or electric migration (Fan *et al.* 2010). Another technique called vitrify technique wherein the polluted soil is subjected to heating at high temperatures 1400~2000°C, during which the organic compounds will be decomposed or volatilized and the steam produced as well as pyrolysed products will be collected by off-gas treatment systems; once after losing the temperature the products forms rock shape vitreous sieges bounding the immobilized metals.

Altogether, physical and chemical remediation methods have many limitations including; irreversible alteration in soil properties, alterations in soil microflora, secondary pollutions as well as these methods are generally expensive and need intensive labour, which make them a inappropriate solution to solve this problem

(Zubair *et al.* 2016; Jegatheesan *et al.* 2016). In contrast, the biological remediation is appropriate, cost-effective and needs less management; it includes microbial remediation, animal remediation and phytoremediation. Generally the microorganisms cannot directly degrade HMs, but it influences their migration and transformation by altering physicochemical status; the main mechanism includes precipitation, complexation, oxidation/reduction, extracellular complexation and intracellular accumulation. Besides, microbial leaching is very efficient technique for extracting valuable metals from low-grade ores and mineral concentrates; however, their efficiency mainly influenced by various factors such as pH, moisture content, temperatures and oxygen levels, and sometime their selective interactions with some contaminants may incur secondary pollution to the environment as well.

Animal remediation is based on the characterization of some lower animals that has the capacity to adsorb, degrade or to migrate HMs in order to reduce or remove the toxicity levels to the environment. For instance, the earthworms are efficiently utilized for reclaiming the HM polluted soil. Kou *et al.* (2008) reported that the efficiency of Pb accumulation by earthworm when testing earthworm on Pb contaminated sites; also acknowledged the accumulation rate was found to be increasing with the increased Pb concentration in soils.

The recruitment of living plants in fixing or adsorbing metal contaminates in order to clean up the environment is termed as phytoremediation. When compared to their physical and chemical counterparts, phytoremediation offer an efficient, environmental friendly and cost-effective technique. Since last three decades, it gained public attention and other regulatory support in soil reclamation. These techniques are broadly divided into three such as phytostabilization, phytovolatilization and phytoextraction (Glick 2010).

Phytostabilization referred to the fixing of metal pollutant by plants via adsorption, oxidation/reduction and precipitation, thus reducing their bioavailability and migration into food chain and water table (Wang *et al.* 2009). Whereas, in phytoextraction, the metal tolerant/ hyper accumulator plants adsorb, translocates and further process the HM contaminants in the above ground plant part. Naturally, scientists consider phytostabilization more suitable and practical than other phytoremediation techniques for its long-term service as vegetation coverage (Mendez *et al.* 2007).

It was estimated that the remediation of tailings using conventional techniques such as chemical stabilization, capping and excavation are very expensive and costs almost 130,000 to 1,600,000 \$US ha⁻¹ (Berti and Cunningham 2000). Hence, the phytoremediation takes up the place with the recognition of its potential as well as they are less expensive when compared to the conventional techniques; in general it costs about 60,000 to 300,000 \$US ha⁻¹ and also stood as minimal environmental damages (Kidd *et al.* 2009).

5. Importance of phytostabilization in mine tailings

Phytostabilization creates a vegetative cap for the long-term stabilization and containment of the tailings. The plant stabilizes the metal contaminants by various means in various plant parts; for instance, the canopy reduces aeolian dispersal and the roots apart from preventing through water erosion, it stabilizes metals either by adsorption and accumulation or restraining in rhizosphere by precipitation and complexation. Over and above, the establishment of plants in tailing areas intensifies the heterotrophic microbial community composition assisting plant growth and metal stabilization (Glick 2003; Mendez *et al.* 2007). The phytostabilization focuses on sequestration of metal contaminants within rhizosphere boundaries thus restricting their translocation to plant parts in contrast to phytoextraction (Ernst 2005). Further it makes the metal contaminants to be less bioavailable to the higher animals and human beings marking its significant in food chain; preventing biomagnification (Wong 2003). Since mine tailings are not suitable for growing plants due to having several adverse features, addition of organic or inorganic amendments in phytostabilization process is very common to immobilize metals in situ as well as to improve soil health for facilitating plant growth and survival and such assisted phytostabilization approach often referred to aided phytostabilization (Mench *et al.* 2006; Vangronsveld *et al.* 2009). Selection of appropriate plant species is the major issue to make any phytostabilization process successful. As reported in the previous studies, plant species that are deep rooted, capable to produce high biomass, tolerant to high concentrations of metals, translocate less metals from roots to above-ground parts and able to adapt with poor soil nutrient found to be suitable for phytostabilization (Pulford & Watson 2003). Aided phytostabilization, besides employing plants alone, the application beneficial amendment in order to enhance the phytostabilization practices is very useful strategy to deal with the mine tailing reclamations (Lee *et al.* 2014).

Additionally, these strategies can help in stabilizing the environment by two means; 1) the added amendments alter the physicochemical status of metal contaminants by various means of adsorption/ absorption, complexation and speciation in a way to prevent their bioavailability, 2) the established vegetation may improve soil physicochemical and biological parameters in order to restore normal soil functioning of metal-polluted areas in the long term (Bolan *et al.* 2011) and with progression of time may convert tailings materials into soil (Mendez & Maier 2008). Aided phytostabilization also confer the containment of metal contaminants within the vadose zone by complexation and precipitation within rhizosphere or accumulating in roots thus preventing the mobilization of HMs via wind, soil dispersion, leaching and water erosion (Bolan *et al.* 2011). Selection of native plants for phytostabilization practices are very much appropriate as the plants can ensure their growth establishments since

they have evolved survival mechanisms that fits to that particular environment; secondly by avoiding non native plant species will further helps in avoiding the establishment of potentially invasive species that may affect local plant diversity. Selection of a plant variety for revegetation is the key factor in phytostabilization; various perennial grasses, shrubs, and trees are preferable. The grasses may give a quick cover to the ground and limits the aeolian dispersal within the due time taken for establishment by shrubs and trees (Williams & Currey 2002); contrarily, the shrubs and trees can strengthen the remediation by establishing stronger root system that prevent erosion and extensive dense canopy cover to prevent dispersal by air over the long term. Hence, recruiting these plants and establishing on mine waste along with aided amendments can help in achieving the phytostabilization through various means of complexation, precipitation, sorption and accumulation in root tissues (Mendez & Maier 2008; Mirza *et al.* 2011). Moreover, usage of woody plants permits soil structure development besides offering thick vegetation cover and erosion control; it also minimizes the leaching and efficient utilization of ground water and nutrients (Zhang *et al.* 2011). Normally, the tailings are poor in organic matter and nutrient levels to support vegetation, but through the assisted phytostabilization, organic matter can be introduced by various amendments such as plant residues, compost, biochar, animal manure, municipal waste, peat, woodchips, sawdust and other industrial residues (Li & Huang 2015); which may also improve soil structure, water holding capacity, nutrient content and cation exchange capacity.

6. Use of different amendments to facilitate phytostabilization of mine tailings

Normally, the mine tailing are characterized as unfavorable environment for plant establishments due to their extreme physicochemical conditions such as extreme pH, high salinity, poor water retention capacity, high concentrations of HMs, and less soil organic matter and often infertile (Asensio *et al.* 2013a). In order to establish plant growth in such poor environment, it is always needed to improve the physicochemical characteristics by amending various organic and inorganic additives (Courtney *et al.* 2009), which may also serves as an attempt in soil amelioration.

Various organic amendments have been already employed in reclamation of tailings includes composts (kitchen wastes, garden waste, olive mill waste, animal wastes, spent mushroom), biosolids (sewage sludge, sanitary wastes, food wastes), manures (goat, cattle, pig, poultry), biochars (crop straw, hardwood, tea waste, fruit waste), slurry (pig, cattle) and peat (Park *et al.* 2011; Bolan *et al.* 2014; Karna *et al.* 2017). These amendments can be used alone or in combination with the other amendments of same/different sources (Bolan *et al.* 2014) and/ or sometimes added along with other inorganic materials (especially of alkaline) such as lime stones, marble waste, hydrated lime, red mud and phosphate fertilizers (Pardo *et al.* 2014, 2016; Karna *et al.* 2017). The addition of lime in order to neutralize/ reduce the toxicity of metals is a generally adopted method in reclaiming oxidized mine tailings (Catalan *et al.* 2002); however, the main limitation of liming amendments are their dissolution and leaching phenomenon in some strong acidic environments (Ruttens *et al.* 2010). Moreno *et al.* (2004) documented the use of pumice as inorganic amendment to improve the drainage of fine-grained tailings. Also, the use of phosphate-based materials is reported to be useful in immobilizing HMs in soil (McGowen *et al.* 2001).

The rate of addition of inorganic fertilizers are of important concern in case of selecting a native vegetation for phytostabilization practices of tailings in arid and semi arid environments, since the vegetations are already accustomed to establish its growth under low nutrient condition, so excessive fertilizer input may tend to change the plants to respond differently (Piha *et al.* 1995). Phosphate fertilizers are exceptional, which is utmost important to alleviate the phosphorous shortage caused by the formation of insoluble metal-phosphates; albeit, the addition of phosphate may sometime increase the arsenic uptake by plants and leaching of mine tailings since their chemical similarities with arsenate (Mains *et al.* 2006).

Altogether, the inorganic additives basically improve few of the physical properties of tailing such as pH, decreases metal solubility, few chemical behaviors and drainage (Janoš *et al.* 2010). Whereas, comparatively the organic amendments proven to improve various soil properties, nutritional levels, water retention capacity along with buffering the pH levels and indirectly affecting the mobility of metals by adsorption and complexation (Tordoff *et al.* 2000).

Recruiting compost as an amendment in phytoremediation trails of mine tailings at Iron King Mine and Humboldt Smelter Superfund sites were studied (Gil-Loaiza *et al.* (2016); results showed at about 41 months 21 to 61% canopy was established in compost amended treatment and there were no plant establishment was reported in unamended tailing soils. As previous study documented, compost amendment and seeding facilitated plant growth and development in preliminary greenhouse studies, and afterwards sustained growth over 4 years suggested feasibility for this phytostabilization technology in the field trial (Gil-Loaiza *et al.* 2016). The biosolids from sludges were used as an amendment for Cu tailings by Asensio *et al.* (2013b) who observed the significant improvements in the biological quality of the soil as well as biological community structures. Another report documented that the application of class A biosolids on the mine tailings increases bacterial growth (Pepper *et al.* 2012).

Biochar, an organic amendment is recently gaining attention for reclamation of polluted environment by

efficient means of immobilization of various contaminants (HMs, organic pollutants) (Ahmad *et al.* 2016). It also improves soil nutrition, soil texture and physiological properties such as pH, EC, CEC and water holding capacity (Fellet *et al.* 2011). Biochar also employed in phytostabilization practices with an aim of stabilizing the toxic metals by limiting their mobility and bioavailabilities as well as improving the vegetation cover by supporting soil nutrition.

The Agricultural wastes (such as crop stalks and animal manure) contain different functional groups such as carboxyl and hydroxyl groups which serve as the suitable sites for metal adsorption (Liu 2017). In addition, addition of organic materials like woodchips, pulp waste, and cattle manure on tailings shows positive effects for the treatment of acid mine drainage (Baker *et al.* 2011; Hulshof *et al.* 2006). Along with low cost and renewable nature, they increase microbial quantity and activity (Seaker and Sopper, 1988).

In addition, many studies reported the positive effects of organic additives (municipal waste, manure compost, biosolid compost and poultry litter) in reducing the toxicity of HM on soil enzymes (Karaca *et al.* 2006; Xian *et al.* 2015). Organic amendments may enhance soil enzymatic activity in many of the ways; (1) intra and extracellular enzymes stimulate microbial activity in the added materials, (2) some of the functional groups of humic acid such as carboxyl, phenolic, alcohol, and carbonyl groups may react with the ions to form metal–humate complexes (metal chelation) in order to stabilize them (Pascual *et al.* 1998). Ameloot *et al.* (2013) reported the increment of dehydrogenase activity (73%) after adding biochar produced at 350°C. Jain *et al.* (2016) also has documented the improved phosphatase enzyme activity of mine spoils after amending organic amendments. Kızılkaya *et al.* (2004) reported that addition of organic matter in treatments increases the CAT activity when compared to the control soil; also suggested a minimum quantity of organic matter is necessary for enzyme activity and the activity increases directly with the increasing rate of organic amendment.

7. Conclusion

Modern civilization is greatly depends on non-ferrous metals because of their intensive usage in manufacturing processes. Hence, in spite of having serious detrimental impacts on environment and human health, it seems to be impossible to stop or reduce the activity of mining industries and thereby generation of hazardous mine wastes like tailings. In this situation, to develop proper management techniques for decontaminating the mine tailings so that we can reduce the harmful effects to the minimum level. As reported, the existing physical and chemical technologies are mostly expensive, often involve in secondary pollution and thus, not feasible specially for large mine wastelands. Recently, scientists suggested phytoremediation as the most feasible practice to remediate mine tailings having high metal load, by which environmental risks associated with such mine wastes can be attenuated as well as creation of aesthetically unpleasant conditions can be avoided. Due to having HMs in high concentrations and poor soil quality, mine tailings are not unfit for growing plants. Therefore, screening out of tolerant native plant species for any particular mine site is the primary challenge. Moreover, considering the need of long-term vegetation coverage on mine sites, phytostabilization attracts the attention of the scientists over phytoextraction. With the development of scientific ideas, aided-phytostabilization is being greatly popularized, where the used amendments help vegetation establishment by decreasing the phytoavailable metal concentrations as well as improving soil quality. Although metal removal or stabilization is the primary goal of any kind of phytoremediation, the success of the process mainly depends on the improvement of plant antioxidant enzymes to enhance plant tolerance and construction of soil functional ability. However, instead of a single method like phytoextraction or immobilizing agents, combined use of several techniques like phytostabilization, amendments and microorganisms might be of more useful. Experiments are necessary to evaluate available bio-waste materials and plant species to facilitate the restoration of mine-spoils having various properties. The research attempts could be extended to molecular studies to find the mechanism of HMs phytostabilization, immobilization and factors governing the translocation in the soil-plant system. Most importantly, long-term field level investigations are needed to evaluate the results of lab and green-house experiments.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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