

# Reduction of Heavy Metals during Composting- A Review

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**Abstract-** Composting is becoming a more acceptable and economical method for treating sewage sludge, municipal solid waste, tannery waste, pig manure, poultry manure, etc.. The application of compost formed by above waste material to land can be used as soil fertilizer/conditioner due to presence of nitrogen, phosphorus, potassium and other nutrients. However, presence of heavy metals in the compost restricts its use as soil conditioner. Heavy metals uptake by plants from the soil and successive accumulation in human tissues and biomagnifications through the food chain causes both human health and environment concerns. Heavy metals from the compost can be reduced by addition of some chemicals (natural zeolite, red mud, lime, sodium sulfide, bamboo charcoal and bamboo vinegar, etc.) and biological agents during composting process. Biological agents such as *Phanerochaete chrysosporium* that is a fungus has been used to remove Lead (Pb) from the compost and earthworm can accumulate the high concentration of heavy metals in the non-toxic forms and be capable of reducing possible toxic effects of unessential heavy metals by utilizing them for physiological metabolism. The principal advantage claimed for biological process over the use of chemicals during composting is the low capital cost. Therefore, the present study gives an overview of the various heavy metal reduction techniques from the composting of various wastes materials carried out by different mode of operation.

**Keywords-** Composting; Heavy Metals; Soil Contamination; Reduction

## I. INTRODUCTION

Composting is an easy technique to manage all types of wastes (such as sewage sludge, municipal solid waste, tannery waste, pig manure, poultry manure etc.) which are biodegradable. The application of compost formed by above waste material to land can be used as soil fertilizer/conditioner due to presence of nitrogen, phosphorus, potassium and other nutrients.

Composting is the process in which organic matter is transformed into compost by aerobic microorganisms, it comprises three major phases: mesophilic, thermophilic and cooling phase (the compost stabilization phase) [1]. It can reduce the solid waste volume by 40-50% [2], pathogens are destroyed by the metabolic heat generated by the thermophilic phase, which degrades a big number of hazardous organic pollutants and make available a final product that can be used as a soil improvement or fertilizer [3]. If the final product contains high level of heavy metals, it often hinders agriculture land application of sewage sludge compost and it may be noxious to soil, plants and human health. Heavy metals uptake by plants and successive accumulation in human tissues and biomagnifications

through the food chain causes both human health and environment concerns [4].

The industrial and municipal solid wastes assigned to be utilized agriculturally and to remove heavy metals from them, a number of techniques have been put forward in many countries, which make use of physical, chemical or biological methods, viz. thermal, extraction, ion exchange and biological leaching methods [5]. According to the procedure of Tessier [6], heavy metals are associated with five fractions: the exchangeable fraction, which is likely to be affected by changes in water ionic composition as well as sorption-desorption processes. A salt solution is commonly used to remove the exchangeable fraction. The carbonate-bound fraction is susceptible to changes in pH; an acid solution is used secondly. Metals bound to Fe and Mn oxides are particularly susceptible to anoxic (reducing) conditions so a solution that is capable of dissolving insoluble sulfide salts is used thirdly. To remove metals bound in the organic phase, the organic material must be oxidized. During the first step of composting there are changes in pH value (acetic acid formation) and in ammonia content (affected by the action of the proteolytic bacterial and by the temperature). The pH changes, which occur in the beginning of the composting process, affect the exchangeable and carbonate fraction. The pH changes may be due to acid formation during the decomposition of organic matter contained in the sludge [7]. The residual fraction consists of metals incorporated into the crystal structures of primary and secondary minerals. This fraction is the hardest to remove and requires the use of strong acids to break down silicate structures [8]. Physicochemical and biological methods, reducing agent and target metals are given in Table I. The present paper gives an overview of the various heavy metal reduction techniques from the composting of various wastes carried out by different modes of operation.

TABLE I PHYSICO-CHEMICAL AND BIOLOGICAL METHODS, REDUCING AGENT AND TARGET METALS

Methods	Reducing Agent	Target Heavy Metals	Authors
Physico-chemical methods	Natural zeolite	Zn, Cu, Ni, Cr, Cd, Pb, Fe, Mn	Zorpas <i>et al.</i> [6]
		Cu, Ni, Cr, Cd, Pb	Sprynskyy <i>et al.</i> [11]
		Zn, Cu, Ni, Cr, Pb, Mn	Stylianou <i>et al.</i> [12]
		Zn, Cu, Ni, Cr, Cd, Pb, Hg	Villasenor <i>et al.</i> [13]

		Cu, Zn, Mn, Co Zn, Cu, Ni, Cr, Cd, Pb Cu, Ni, Cr, Cd, Pb	<i>Erdem et al.</i> <sup>[17]</sup> <i>Chiang et al.</i> <sup>[41]</sup> <i>Kosobucki et al.</i> <sup>[42]</sup>
	Lime and sodium sulfide	Cu, Mn, Ni, Zn Cu, Zn, Ni Zn, Cu, Ni, Cr, Cd, Pb	<i>Fang and Wong</i> <sup>[14]</sup> <i>Wang et al.</i> <sup>[15]</sup> <i>Chiang et al.</i> <sup>[41]</sup>
	Bamboo charcoal and bamboo vinegar	Cu, Zn Cu, Zn	<i>Chen et al.</i> <sup>[16]</sup> <i>Hua et al.</i> <sup>[19]</sup>
	Red mud	Zn, Cu, Ni, Cr, Pb	<i>Qiao and Ho</i> <sup>[21]</sup>
	Coal fly ash	Zn, Cu, Ni, Cr, Cd, Pb	<i>Chiang et al.</i> <sup>[41]</sup>
Biological methods	Fungi	Pb	<i>Zeng et al.</i> <sup>[27]</sup>
	Bacteria	Pb, Cd, Cr, Mn, Mg	<i>Nair et al.</i> <sup>[33]</sup>
	Earthworm	Pb Pb, Cd, Cr, Cu, Zn Zn, Cu, Cr, Cd, Pb, Fe	<i>Liu et al.</i> <sup>[31]</sup> <i>Li et al.</i> <sup>[38]</sup> <i>Gupta et al.</i> <sup>[40]</sup>

## II. REDUCTION OF HEAVY METALS BY PHYSICO-CHEMICAL METHOD DURING COMPOSTING

The thermophilic phase of composting, which is the first step of composting, affects the exchangeable fraction. The oxic and anoxic conditions (produced by acetic acid and ammonia) at the first step of composting, affect the reducible and organic fractions<sup>[6]</sup>. He et al.<sup>[9]</sup> reported the content of exchangeable Pb increased during the later thermophilic stage, but dropped again in the cooling period. The relative percent of residual Zn increased 3.38% during mesophilic and thermophilic phases but decreased 1.07% in the cooling stage. The exchangeable and carbonate Cu only accounted for the small parts of total Cu. Their concentrations increased, although a decrease tendency appeared during thermophilic phase. Amir et al.<sup>[10]</sup> studied heavy metals bioavailability or chemical forms of Cu, Zn, Pb and Ni in sewage sludge composting with straw, composting period was 180 days. This study concluded that the largest proportions of metal was found in the residual fraction and fractions more resistant to extraction indicating that the metals were in more stable forms and are consequently considered unavailable for plant uptake. The amount of potentially bioavailable metals was less than 2%.

Heavy metals contain compost quality can be improved by adding some chemical compounds. Many studies have been carried out by using natural zeolite<sup>[(2), [6], [7], [11] - [13)]</sup> lime<sup>[(4), [14)]</sup>, lime and sodium sulfide<sup>[15]</sup>, bamboo charcoal<sup>[16]</sup>. These chemical compounds used as amendments, which can improve compost quality by removing or

changing mobile and available form of metals to less mobile or residual or less available form. Mobile species of heavy metals cause more serious pollution problems since they can be easily taken up by plants and enter the trophic chain or pollute the ground waters<sup>[11]</sup>. Heavy metals reduction mechanisms of physicochemical and biological methods are given in Table II.

TABLE II HEAVY METALS REDUCTION MECHANISM OF PHYSICO-CHEMICAL AND BIOLOGICAL METHODS

Methods During Composting		Reduction Mechanisms	Authors
Physicochemical methods	Thermophilic phase	The oxidation process and the formation of organo-metallic complexes taking place during composting could reduce the soluble contents of metals. Humic substances bind with exchangeable and carbonate fractions of metals.	<i>He et al.</i> <sup>[9]</sup> , <i>Fang and Wong</i> <sup>[14]</sup>
	Natural zeolite	It has the ability to increase the porosity of the substrate and as a result, to improve the composting process and the biodegradability of the organic matter. It can increase Na and K in compost with exchange with toxic metals. It has the ability to readily take up almost all metals that are bound to the exchangeable and the carbonate fractions.	<i>Zorpas et al.</i> <sup>[6]</sup>
	Lime and sodium sulfide	Lime provided a buffering against the decrease in pH and a suitable amount of Ca, which would improve the metabolic activity during composting. Alkaline lime could neutralize the organic acids released during composting, and thus reduce the formation of metal-organic matter complexes during lime-sludge co-composting. When Na <sub>2</sub> S is added to sewage sludge, the heavy metals are converted to metal sulfides by the sulfidation reaction.	<i>Fang and Wong</i> <sup>[14]</sup>
	Bamboo charcoal (BC) and bamboo vinegar (BV)	BC has a highly microporous physical structure. The porosity is about five times greater and the absorption efficiency ten times higher than that of wood charcoal. BC has a high adsorption capacity for heavy metals and attributed this	<i>Chen et al.</i> <sup>[16]</sup> , <i>Hua et al.</i> <sup>[19]</sup>

		adsorption to the large specific surface area, surface negative charge and high surface density of functional groups and metal oxides of BC. BV played an important role in improving the immobilization of heavy metals; it could stimulate microbial activity during composting. Additionally, humus produced during composting was reported to reduce the mobility of HM successfully through metal–humus complex formation				effects of superfluous heavy metals by utilizing them for physiological metabolism. Metals interact with many chemicals and participate in detoxification processes, as part of the enzymes of the antioxidant systems, such as superoxide dismutase (SOD), and in metallothioneins (MT). The availability of heavy metals decrease due to bioaccumulation of metals and organo-complex formation during this process	<i>Li et al.</i> [38]
	Red mud	Red mud has a high pH, cation exchange capacity, Al and Fe oxides and clay minerals and can effectively adsorb free cations from solution. The addition of red mud and the composting process increased pH to over 7 in the red mud sludge compost. The soluble metals can precipitated as metal hydroxide. The increased pH also enhanced the precipitation of metal carbonates, thus reducing the exchangeable metal concentration. Red mud affects the speciation of heavy metals through increasing the pH, solid-to-solution ratio and available adsorption sites.	<i>Qiao and Ho</i> [21]				
Biological method	Fungi ( <i>Phanerochaete chrysosporium</i> )	<i>Phanerochaete chrysosporium</i> capable of accumulating metal ions in their cells by intracellular uptake and can also chelate metal ions by the carboxyl, hydroxyl or other active functional groups on cell (including the dead cell) wall surface.	<i>Zeng et al.</i> [27], <i>Liu et al.</i> [31]				
	Bacteria	Bacteria excrete a chelating agent called siderophore. Siderophores are specific Fe (III) ligands and are able to bind to other metals, such as magnesium, manganese, chromium (III), gallium (III) and radionuclides, such as plutonium(IV). Siderophores binding to metals, including toxic ones like lead and cadmium.	<i>Nair et al.</i> [33]				
	Earthworm	They are capable of reducing possible toxic	<i>Ghyasvand et al.</i> [35]				

#### A. Reduction of Heavy Metals during Composting Using Natural Zeolite

Zeolites are naturally occurring hydrated aluminosilicate minerals. They belong to the class of minerals known as “tectosilicates” [17]. It occurs as three-dimensional frameworks of  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedral [13].

Natural zeolites and the clinoptilolite in particular seem to be appropriate amendment materials for sewage sludge taking into account their sorption and exchangeable properties towards the heavy metals. Addition of the clinoptilolite rock to sewage sludge might change chemical speciation of heavy metals in composts and decrease their mobility and bioavailability [11]. Zorpas et al. [6] reported that the amount of zeolite added did not affect the total phosphorous and total Kjeldahl nitrogen (TKN) of the final compost. Zeolite as a bulking material has the ability to increase the porosity of the substrate and as a result, to improve the composting process and the biodegradability of the organic matter. Clinoptilolite has the ability to exchange sodium and potassium. With increasing amounts of zeolite in the compost, the concentration of all heavy metals in the samples decreased while the concentration of sodium and potassium increased. Villasenor et al. [13] reported that the zeolites retained 100% of the Ni, Cr and Pb that was present in the sludge. Zeocat was the most effective zeolite for the removal of Cu, Zn and Hg and also reported that clinoptilolite had the ability to take up metals associated with the mobile forms such as the exchangeable and the carbonate fractions. Stylianou et al. [12] determined that clinoptilolites displayed the following metal retention selectivity:  $\text{Zn}^{+2} > \text{Cr}^{+3} > \text{Ni}^{+2} > \text{Cu}^{+2} > \text{Mn}^{+2}$ .

It was observed that clinoptilolite has the ability to readily take up almost all metals that are bound to the exchangeable and the carbonate fractions. Clinoptilolite took up all metals bound in exchangeable and carbonate fractions according to the following selectivity series:  $\text{Cu} > \text{Cr} > \text{Fe} > \text{Ni} > \text{Mn} > \text{Pb} > \text{Zn}$  [6]. Sprynskyy et al. [11] concluded that the addition of the natural clinoptilolite to the sewage sludge led to the metals contents fall in all four fractions of the sequential procedure. Concentrations of mobile forms of cadmium, chromium, copper and nickel decreased by 87, 64, 35 and 24%, respectively, as a result of

the addition of 9.09% of the clinoptilolite. The total decreases of the metals after 9.09% clinoptilolite addition to the sludge were around 11, 15, 25, 41 and 51% for copper, nickel, chromium, cadmium and lead, respectively. The clinoptilolite rock may be considered as a suitable material to heavy metals immobilization by their bond into firmly sorbed forms of the pseudo residual fraction.

Zorpas et al. [12] concluded that the 25% w/w addition of zeolite in compost is sufficiently removing heavy metals, 12% of Co, 27% of Cu, 14% of Cr, 30% of Fe, 40% of Zn, 55% of Pb and 60% of Ni. The particle size of the clinoptilolite seems to affect the uptake of heavy metals. The metals concentration was taken up from the clinoptilolite increases with the particle size of clinoptilolite increases. This observation could be explained by the effect of surface dust, which clogs pores and causes structural damage in smaller particles, due to the grinding process.

Stylianou et al. [12] reported that the zeolite has ability to trap metals by ion exchange and adsorption processes. The content of zinc is decreased by 94.1%, of copper by 59.5%, of chromium by 82.2%, of nickel 69%, while in the case of Mn the respective percentage is 48.1%. To sum up, the order of metal uptake from zeolite is:  $Zn^{+2} > Cr^{+3} > Ni^{+2} > Cu^{+2} > Mn^{+2}$ . Through the composting process the break-up of organic matter (OM) increases the presence of metals in the exchangeable form and helps natural minerals, such as zeolite, to adsorb them. This behavior helps the immobilization of metals.

Hydration of the cation is also important. For example, in clinoptilolite-water ion exchange systems the series found is:  $Pb^{2+} > Cr^{3+} > Fe^{3+} > Cu^{2+}$  and  $Pb^{2+} > Zn^{2+} > Cu^{2+}$ . It should be noted that OM in soluble and insoluble forms plays contrasting roles in controlling total soluble metals. OM promotes the dissolution of Cu, Zn and other metals by building organic complexes. It is reported that the addition of organic matter increased the solubility of metals by the formation of organometallic complexes [11]. The percentage of Cr is higher in organic phase during the thermophilic phase than the other fractions. After the thermophilic phase, Cr seems to be transferred to the residual fraction while at the end of the maturity period (after 150 days) zeolite binds all of the readily available metal (metals which are associated with mobile forms) [7]. Chromium content has also decreased most after the zeolite addition in the first fraction (by 49%) [11].

#### *B. Reduction of Heavy Metals during Composting Using Lime and Sodium Sulfide*

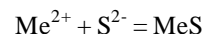
Lime is considered as one of the most common amendment materials for sewage sludge stabilization, as it plays significant role in reducing the microbial content of sludge (pathogens), as well as the availability of heavy metals, enhancing the agricultural benefits and lowering the respective environmental risks [18]. A slower rise in temperature was observed in sludge with lime amendment as compared to that of the control with sludge only. The small amount of lime added provided a buffering against the

decrease in pH and a suitable amount of Ca, which would improve the metabolic activity during composting [14].

Chemical forms of metals might be affected in general by the pH, the presence of organic matter, etc. The residual zinc might be transformed mainly into the oxidizable and marginally to other forms of zinc during the stabilization and ageing process; however, increased residence time and lime addition may reduce this transformation [18]. Addition of lime caused a significant reduction in water-soluble Cu, Mn, and Zn contents at the beginning of composting and this effect became more obvious as composting proceeded [14].

Wong and Selvam [4] reported that the addition of lime did not cause any marked changes in the form of Cu during composting. However, the exchangeable, acid extractable and reducible fractions increased marginally after composting and the addition of lime reduced this transformation. Since the stability constant of Cu complexes with organic matter is high, the organic bound fraction (oxidizable) was reported as the major fraction of Cu by many researchers. Wang et al. [15] reported that the addition of sodium sulfide and lime (SSL) did not cause marked changes in the form of Cu during composting. However, the organic matter and sulfide bound Cu increased from 62.9% in control compost to 65.3% in the SSL amendment compost. Alkaline lime could neutralize the organic acids released during composting, and thus reduce the formation of metal-organic matter complexes during lime-sludge co-composting. The increase of organic matter and sulfide fraction is mainly because of the conversion of heavy metals to sulfides.

Wang et al. [15] also reported that the residual fraction of Zn was the dominant fraction in the lime treated compost at 1% and 1.63%. The exchangeable and carbonate bound fractions decrease from 10.0% and 27.5% in sewage sludge to 1.5% and 8.5% in SSL amendment compost, respectively. From these studies, it can be concluded that the SSL amendment is significant in reducing the mobile and easily available fractions (exchangeable and carbonate bound Zn) of the co-compost. It could be concluded that the carbonate bound, Fe-Mn oxide bound and organic matter and sulfide Ni were transformed mainly into residual forms of Ni during composting. The addition of SSL caused an increase in organic matter and sulfide fraction (27.8%) compared to that in the control, which might also be mainly because of the formation of NiS, by the sulfidation reaction expressed in following Equation:



#### *C. Reduction of Heavy Metals during Composting Using Bamboo Charcoal and Bamboo Vinegar*

Bamboo is a renewable bioresource when the cycle of its plantation and use is properly managed. Pyrolyzing bamboo under oxygen limited conditions produces bamboo charcoal (BC). BC has a large amount of micropores and an extremely large surface area, about 4 and 10 times greater than those in wood charcoal, respectively. Bamboo charcoal may be an ideal amendment for nutrient conservation and

heavy metal stabilization due to its excellent adsorption capability<sup>[19]</sup>.

Bamboo vinegar (BV) is a brown-red transparent liquid produced during pyrolysis of BC and contains more than 200 types of chemical components, in which acetic acid is the main component<sup>[16]</sup>. Chen et al.<sup>[16]</sup> concluded that the addition of BC or BC + BV into pig manure (PM) composting materials influenced temperature and pH changes. It shortened the time needed to enter the thermophilic phase, decreased pH at the thermophilic phase. The addition of BC or BC + BV reduced TKN loss and mobility of Cu and Zn in PM composting materials. TKN loss was reduced by 74% in the 3% BC + 0.4% BV treatment. The mobility of Cu and Zn was reduced by 35% and 39% in the 9% BC treatment. These results indicate that the addition of BC or BC + BV into PM composting materials is an effective method to reduce negative effects of PM composting.

Hua et al.<sup>[19]</sup> concluded that mobility of heavy metals in the sludge composting could also be reduced by the addition of BC. However, the stabilization effect of BC was different for  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ . DTPA-extractable contents of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  in sludge composting material with 9% BC amendment dropped 27.5% and 8.2%, respectively, at the end of composting as compared with that of the non-BC control. There was no significant difference in the ability of fresh BC compared to composted BC to retain either  $\text{Cu}^{2+}$  or  $\text{Zn}^{2+}$ , indicating that composting had little effect on the adsorption capacity of BC for these heavy metals.

#### *D. Reduction of Heavy Metals during Composting Using Red Mud*

An industrial waste by-product that could potentially be used for remediation of heavy metals is red mud. Red mud is produced during the refining of bauxite to alumina through the Bayer's process<sup>[20]</sup>. It is composed of hematite ( $\text{Fe}_2\text{O}_3$ ), boehmite ( $-\text{AlOOH}$ ), quartz ( $\text{SiO}_2$ ), sodalite ( $\text{Na}_4\text{Al}_3\text{Si}_3\text{O}_{12}\text{Cl}$ ) and gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) [20]. Red mud addition generally reduces metal leachability and therefore the potential hazard of releasing metals from sludge compost through adsorption and complexation of the metals on to inorganic components to different extents for the different metals<sup>[21]</sup>.

Qiao and Ho<sup>[21]</sup> concluded that red mud addition reduces the leachability, plant availability and total metal content. The effect of red mud is different for each metal with a greater effect on Cr, Pb and Zn speciation than on Cu and Ni speciation. More than 80% of Cu is tightly bound to the organic fraction, and red mud addition hardly affects the Cu speciation. Although the red mud increases total Cr in sludge compost, the leachable and plant available Cr are undetected in the red mud compost. The Cr remains in tightly bound fractions, and thus is unlikely to be released into the environment.

### III. REDUCTION OF HEAVY METALS BY BIOLOGICAL METHOD DURING COMPOSTING

The way of removing heavy metals from compost is by chemical means, i.e., by leaching with solutions of sulfuric acid and nitric acid. Such techniques can be very expensive and may have several disadvantages, such as unpredictable metal ion removal, high reagent requirements, and the generation of toxic sludges, which are often difficult to dewater and may require extreme caution when disposing of them. Development of cost-effective alternatives, such as biosorption, bioaccumulation, and bioleaching has become an intensive area of exploitation over the past decade. Microbial biomass has been screened for its sorption capabilities<sup>[22]</sup>. The property of nonliving microbial biomass to accumulate heavy metal ions, a non-metabolically driven process called biosorption, the term bioaccumulation described an active process where the removal of metals requires the metabolically activity of living organism<sup>[23]</sup>. Bioleaching processes defined as the mobilization of metal cations from insoluble ores by biological oxidation and complexation processes<sup>[24]</sup>.

Mechanical treatment by grinding, mixing, and sieving out non degradable or disturbing materials (metals, plastics, glass, stones) gives good conditions for biological treatment of compostable materials<sup>[25]</sup>. Microorganisms like bacteria, fungi, algae and yeast are known to tolerate and accumulate heavy metals<sup>[26]</sup>. The microorganisms able to absorb and detoxify heavy metals have been applied to the treatment of metal-contaminated wastewater and could be expected to immobilize metals in solid waste<sup>[27]</sup>. Bioadsorption mechanism involved in the process may include ion exchange, coordination, complexation, chelation, adsorption, micro-precipitation, diffusion through cell walls and membrane which differs depending on the species used the origin and processing of the biomass and solution chemistry<sup>[26]</sup>. Microbial communities play an important role in the detoxification, stabilization and transformation of Cr in the composting material to ensure the environmental sustainability<sup>[28]</sup>.

#### *A. Reduction of Heavy Metals during Composting Using Fungi*

White-rot fungi have generally been found useful in absorbing heavy metal ions from dilute solutions or wastewater with their mycelium<sup>[27]</sup>. White-rot fungi can concentrate metals taken up from substrate in their mycelia<sup>[29]</sup>. It has been reported that *Phanerochaete chrysosporium* is good at absorbing metal from dilute solutions by its mycelium and less Pb ion transferred and it has ability to grow in both solid and liquid environment and degrade a wide range of xenobiotic effectively even in the nutrient-limited condition<sup>[30]</sup>. Heavy metals presented in the environment can directly interact with extracellular enzymes of fungi<sup>[29]</sup>.

Preference of living biomass of metal binding ion depends on nutrient, environmental condition and cell age<sup>[26]</sup>. Nonviable biomass has several advantages for metal biosorption from solution, especially as there is no requirement for maintenance and nutrition<sup>[22]</sup>. Composting of Pb-polluted waste by fungi with the ability of immobilizing Pb as a promising method also needs further studies. *Phanerochaete chrysosporium* has been used to

remove Pb ions in wastewater because it is capable of accumulating metal ions in their cells by intracellular uptake, as many researchers validated, and can also chelate metal ions by the carboxyl, hydroxyl or other active functional groups on cell (including the dead cell) wall surface [31].

Zeng et al. [27] reported that almost 70.5% of Pb was bound to the residual fraction in Reactor C (contain spore suspension of white-rot fungus) and 58.7% in Reactor B (without spore suspension of white-rot fungus). After 80 days of composting, the content of the exchangeable Pb in Reactor C even dropped to 0%, while that in Reactor B remained 2.86%. The results showed that the bioavailability and transfer ability of Pb in Reactor C were lower than those in Reactor B. As a result, the potential hazards of compost in Reactor C were lower than those in Reactor B, which indicated that composting Pb-contaminated solid waste with white-rot fungus could control the phytotoxicity of Pb to some extent. Reasons for these results might be as follows: (i) white-rot fungi could chelate with Pb by the carboxyl, hydroxyl or other active functional groups on cell wall surface, (ii) white-rot fungi could improve the composting process, as proved by the data obtained in this study and reported previously. The humus formed could also bind Pb stably.

Liu et al. [31] proved that the composting methods without inoculants and with inoculants of *Phanerochaete chrysosporium* could effectively transform Pb fractions, reduce active Pb and alleviate the potential harm of Pb-contaminated waste. The transformation behavior of Pb fractions might result from the fact that the Pb ions could be accumulated by fungal mycelium and chelated by the humus formed in the composting. The content of soluble-exchangeable Pb was positively correlated with pH value and microbial biomass, indicating that increasing pH and microbial biomass were important to the immobilization of Pb during composting. Furthermore the better immobilization effect of active Pb was found in the composting method with inoculants (*Phanerochaete chrysosporium*) compared without inoculants, which might be due to the more microbial biomass and higher pH value in composting of Pb-polluted waste with inoculants. It was also observed that the inoculants might be responsible for the increase of the content of residual Pb content during composting.

#### B. Reduction of Heavy Metals during Composting Using Bacteria

The thermophilic bacteria in solid waste compost mainly belonged to the genus of *Bacillus* and there was a shift from several *Bacillus* species to one single *Bacillus* species, i.e., *B. stearothermophilus*, as the major dominant species when the temperature was higher than 65°C whereas *Thermus* strains played an important role in organic matter degradation during the thermogenic phase (>70°C) of the composting process [32].

Siderophores are class of microbial chelating agents, which are low molecular weight ligands synthesized and excreted by bacteria for capturing and supplying iron to support metabolic activity [33].

Bioleaching process has been reported to be an efficient and economical method for the removal of heavy metals from the sludge. The process has also been applied successfully for remediation of soils, sediments, industrial wastes and solid wastes contaminated with heavy metals [34]. The predominant metal-sulfide-dissolving microorganisms are extremely acidophilic bacteria (meaning organisms thriving at pH values below 3) that are able to oxidize either inorganic sulfur compounds and/or iron (II) ions. The classical leaching bacteria now belong to the genus *Acidithiobacillus* (formerly *Thiobacillus*) [24]. Bioleaching process uses the catalytic effect produced by the metabolic activities of iron-oxidizing and sulfur-oxidizing microorganisms resulting in an acceleration of the chemical degradation of the sulfides. It is a low cost and environmental friendly technique which is 80% cheaper in terms of chemical consumption compared to the traditional chemical methods employed for metals leaching from the sludge and recovery of metals from the leachate [34].

#### C. Reduction of Heavy Metals during Composting Using Earthworm

Vermi-composting is a new and useful technology that recently used for recycling the organic part of these wastes [35]. Vermi-composting is a better way of waste conversion since it makes quality manure from primarily organic waste mixtures quickly and gives a nutritionally rich and biologically more active product at reasonable cost. During vermicomposting, earthworms maintain aerobic conditions in waste pile through burrowing and inverting and biochemical processes are enhanced by microbial decomposition of the substrate in the earthworm intestine [36].

During vermicomposting earthworms eat, grind, and digest organic wastes with the help of aerobic and some anaerobic microflora, converting it into a much finer, humified, microbially active material [37]. Vermicomposting is the usual method that managed by earthworms and in addition to decomposing of organic waste, the availability of heavy metals like Pb and Cd decrease due to bioaccumulation of these metals and organo-complexformation during this process [35]. Li et al. [38] showed that *E. fetida* can accumulate Cu, Zn, Pb and Cd. The adult earthworm was speculated to have such an ability to store high concentrations of heavy metals in the non-toxic forms.

Introduction of earthworms for vermicomposting tended to increase the solubilisation of Fe, this behaviour was attributed to a greater rate of degradation in the presence of higher concentrations of different microorganisms within earthworm intestine [39]. It is reported that soluble and exchangeable metal concentrations were the best descriptors of bioaccumulation in *E. fetida*. Tubifex, one of the oldest described aquatic oligochaetes, was able to sequester superfluous Cd in the granules fraction and by proteins as metallothionein-like proteins in the heat stable fraction [38]. The soluble-exchangeable Pb content decreased as the pH increased. The pH is known to affect the ionic form and chemical mobility, so a high pH value can decrease the solubility of metals in the medium [31].

## IV. CONCLUSION

The disposal of wastes (sewage sludge, MSW, tannery waste and poultry waste) on land as a fertilizer is associated with environmental problems due to the presence of heavy metals. During the composting process, the metals content can be reduced by addition some chemicals, microbial inoculants and earthworm. In comparison to other chemicals, natural zeolite is a good amendment because it has ability to exchange sodium and potassium with toxic metals. The inoculation of microorganisms could be very useful to improve the composting process by enhancing enzymatic activity and quality level of the compost is acceptable, with very low heavy metal content. During the vermicomposting earthworm can accumulate the high concentration of heavy metals in the non-toxic forms and capable be reducing possible toxic effects of unessential heavy metals by utilizing them for physiological metabolism. The principal advantage claimed for biological process over the use of chemicals during composting is the low capital cost.

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