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In-situ stabilization of cadmium contaminated soil by using industrial by-products

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Abstract
In situ remediation of heavy metal contaminated soil is extensively stabilized by using chemical released as industrial by products like limestone, red-mud and furnace slag etc. In our study, we tested the effect of red-mud and furnace slag amendments on extractability of cadmium (Cd) heavy metal, phytoavailability by using Indian mustard cv. Pusa Vijay (NPJ-93) and microbial activity of soil after addition of red-mud and furnace slag in soil sample. In situ remediation of contaminated soil by industrial by products was accompanied by increased microbial activity, increase in soil pH and decreased plant uptake of Cd. Soil microbial activity was determined by using microbial parameters like soil respiration, dehydrogenase activity, glucose mineralization and urease test which was found to be significantly increased after red-mud and furnace slag-amended soils. Compared to non-amended soil, only 30% of Cd was detected in red-mud and furnace slag treated soil samples. In the same time, photosynthetic efficiency of mustard plant also increased as compared to non-amended soil.

Key Words: cadmium contamination, in-situ remediation, red-mud, furnace, mustard

Introduction
Cadmium contamination of agricultural and non-agricultural soil is a worldwide problem now a days that affect many sites (Yin et al., 2015) [18]. Accumulation of Cd in agricultural soil by any means adversely affect food quality, environment and soil health (Douay et al., 2008) [6]. Cadmium from contaminated soil ultimately reaches to all tropic levels affecting the entire living organism from microbes to human. To remediates the Cd-contaminated soil, many technologies have been developed by environmentalist (Grey et al., 2006) [9].

Ex-situ soil-remediation by transportation, thermal treatment, soil washing, land filling and phytoremediation of contaminated soil are highly effective technologies but these are with low efficiency, expensive to implement (Basta and McGowen, 2004) [1]. Thus there is a great need of cost-effective, low-input, environmentally friendly innovation for Cd contaminated soil remediation (Lombi et al., 2002) [12]. One acceptable technology is the in-situ stabilization of Cd-contaminated agricultural soil is by the addition of various amendments from industrial by-product like red-mud and furnace slag. (Oste et al., 2002; Basta and McGowen, 2004) [1]. As compared with ex-situ remediation strategy, the above in-situ technology may provide long term solution through the formation of low-soluble minerals or precipitates.

In situ stabilization of heavy metals involves the reduction of metal availability and mobility, either by precipitation or increased absorption. Application of industrial by-products as soil amendment may decrease the availability of heavy metals and ultimately reduces the harmful effects on microorganism, plants, animals and humans (Lombi et al., 2002) [12]. Time to time numerous chemical amendments have been proposed and tested for successful in-situ stabilization of heavy metals from agricultural soil like zeolites (Oste et al., 2002), red-mud (Grey et al., 2006) [9], phosphate (Basta and McGowen, 2004) [1], limestone (Geebelen et al., 2003). According to some research articles, red-mud and furnace slag which are generated in large amount during the extraction of alumina from bauxite following the Bayer process (annually 9 Mt of red-mud), are found to be very effective soil amendment for Cadmium stabilization (Sang-Hwan Lee et al., 2009). It was reported that red-mud and furnace slag amendments shift heavy metals from exchangeable to Fe-oxide fraction and increase their precipitation (Lombi et al., 2002) [12]. In situ stabilization of heavy metals by industrial by products may also beneficial for soil micro florae by decreasing liable element pools of heavy metals. Recovery of in-situ stabilized soil should be assessed by determining soil chemical characteristics as well as measuring the restoration of soil micro florae (Brown et al., 2005). Chemical data itself is not sufficient to check the toxic effect of soil pollutants as they don’t provide the information about the interaction among the contaminants, soil micro florae and soil matrix (Leitgib et al., 2007). According to some research group, soil microbiological and biochemical status are found to be very sensitive indicator of ecological stresses (Perez-de-Mora et al., 2005; Hinojosa et al., 2008) [10].

In the present research article, effectiveness of red-mud and furnace slag was determined to reduce the availability of cadmium in soil and response of biological indicators like plant growth, plant metal uptake and microbial activity to soil amendments.

Materials and Methods

Soil and soil amendments: Cadmium contaminated soils used in this study was collected from the textile industrial zone of Panipat, Haryana, India. Soil samples were dried in hot air oven and mixed completely with the help of a mixer and screened through 2mm sieve before experiment. Physio-chemical properties of the soil was determined and described in table 1. Soil texture was determined using pipeting method described by Gee and Bauder, 1986. pH and electrochemical conductivity was determined by dissolving 1 part soil in 5 part autoclaved distilled water and it was found to be 5.8 (Thomas, 1996) [17]. Soil amendments like red-mud and furnace slag was collected from alumina refinery and steel works, Panipat, Haryana, India respectively. X-ray diffraction analysis showed that red-mud was mainly composed of $Ca_3Al_2 (SiO_4) (OH)_8$, $Al(OH)_3$, Ca_2SiO_4,, $CaAl_2Si_2O_8.4H_2O$, Fe_2O_3, and Al_2O_3. pH of the red-mud was observed to be 11.42. Soil amendments were applied to the Cd contaminated soil at 2% and 5% w/w ratio. For the better experiment set up, soil amendments were reduced to a particle size of <2 mm. 1.5 kg of soil mixture were transferred per pot to determine the mustard plant growth analysis and three identical pots were prepared for both soil amendment treatment. Non-amendment soil was also used as a control soil and was collected from farm ward of Baba Mastnath University, Haryana, India. Both the amendments were completely mixed with experimental soil to obtain homogeneity and then equilibrate for one month. During that time, soil moisture were maintained and mixed properly at intervals of week.

Contaminant extractability

Stabilization of Cd contaminated soil by amendment was checked by using double distilled water and 0.1 M $Ca(NO_3)_2$ (Scott-Fordsmand et al., 2000) [16]. Procedure involve the addition of 3g soil mixture into 30ml double distilled water in a 50ml Tarson centrifuge tube (Tarson Pvt Ltd), thoroughly mixed followed by centrifugation for 20 min at 5100g on a fixed angle rotor and then filtered through Whatman Syringe filter (0.7 µm). Extraction with 0.1 M Ca(NO3)2 solution was performed according to the procedure of Conder et al. (2001) [4] to measure Ca(NO3)2-extractable metals: 1 g soil was combined with 0.1 M Ca(NO3)2, mixed in a shaker, centrifuged for 20 min at 5100 g, and then filtered through Whatman GF/F 0.7-lm borosilicate glass filters.

The availability of Cadmium to human gastrointestinal system in cadmium contaminated soil was determined by using the protocol described by Geebelen et al. (2003): 0.35 g soil was shaken (30 rpm) with synthetic gastric solution (0.4 M glycine; pH 2.2) for 1 h at 37° C, and then filtered through Whatman GF/F 0.7-lm borosilicate glass filters.

Microbial activity: After one month of equilibration, soil sample were taken to determine the microbial activity of stabilized soil. Before analysis, soil samples were kept moist at <4°C to optimum microbial activity. Soil microbial activity before equilibration was analyzed and used as a control. Soil microbial biomass was determined indirectly by measuring the substrate induced respiration in a closed vessel at 20°C. Glucose was added to equilibrated soil at 4mg/g soil concentration followed by incubation for 4 hours at 20°C. CO_2 was generated during the respiration and absorbed NaOH solution and then quantified by titration with 0.05 M HCl (Hydrochloric acid). Soil respiration was measured by calculating CO_2 production at 25°C without glucose addition.

Soil urease and dehydrogenase activity: Soil urease and dehydrogenase activity was determined by protocol described by Kandeler (1995) [15] and Casida (1964) [3] respectively.

Plant growth analysis: After one month of incubation, Indian mustard seedlings were grown in each pot along with ¼ liquid Murashige and Skoog (MS) basal medium. Before transferring to pots, mustard seeds were surface sterilized and germinated over plant tissue culture medium under sterilized conditions. After 20 days, shoots were harvested from pots, washed with double distilled water, oven dried at 60°C over night and then ground to pass through a 1mm sieve. Cadmium concentration in mustard plants were measured by the protocol described by Zheljazkov and Nielson.

Statistical analysis

All the values obtain from soil microbiological and biochemical analysis were reported as mean of three replicates i.e. all the assays were repeated three times under same conditions. Analysis of quantitative variables was done by one-way ANOVA test. Newman-Keuls correlation was used to find out the interaction between two Variables. *p* value <0.05 were considered as statistically significant. Variance was used to determine the significance of regression models.

Results

Soil pH: After the addition of soil amendments, pH increases significantly ($p<0.05$; Table 1) from 5.8 to 7.9 and 8.5 in 5% Red mud and 5% furnace slag respectively.

Table 1: Soil physico-chemical properties

Parameter	Soil	Red-mud	Furnace slag
pH	5.8	11.53	11.25
Total carbon (%)	2.6	-	-
Total nitrogen (%)	0.05		
Cd (mg kg^{-1})	9.7	2.2	1.9
Fe oxides	-	28.5	22.6

Mean values and standard deviations of three replicates.
Soil pH measured at the ratio of soil to H_2O as 1:5 (mass:volume).
Fe oxides were analyzed by citrate and Na-dithionite extraction method.

Soil microbial activity

As compared to non-amended soil (control soil), significantly more CO_2 was evolved and activity of dehydrogenase and urease enzymes was found to be elevated in case of both red-mud and furnace slag amended soils (p<0.05, Table-2). No significant difference was detected in microbial biomass and microbial activity in non-amended soil.

Table 2: Soil microbial activities in soil with different concentration and types of amendments

Treatments	Microbial biomass ($mgCO_2Ch^{-1}100g^{-1}$ soil)	Respiration (mg CO_2 100 g^{-1} soil)	Soil enzymes	
			Dehydrogenase (mg TPF kg^{-1} soil)	Urease (mg NH_4^+ kg^{-1} soil)
Control	235	9.4	70	971
RM 2%	250	23	98	899
RM 5%	245	21	89	889
FS 2%	280	14	69	592
FS 5%	436	13	72	869

Means ($n=3$) followed by same letter within a row are not significantly different ($p>0.05$).
RM, Red-mud; and FS, Furnace slag.
DHA, dehydrogenase, URE, urease
TPF, triphenyl formazan; NP, nitrophenol.

Plant growth parameter

No significant differences were detected in plant growth except some treatment of furnace slag. Some treatment of furnace slag results in increase biomass of mustard seedlings as compared to control seedlings. 5% furnace slag treatment produces a significantly (p<0.05) higher shoot yield than did the other treatments. As compare to non-amended soil, 5% furnace slag soil produces 80% more shoot biomass.

Compared to the control soil, the furnace slag and red-mud treatment significantly (p<0.05) decreased the concentrations of cadmium heavy metals in mustard seedlings. Compared to non-amended soil, 13–29% of Cd was translocated to mustard shoots in the furnace slag and red-mud-amended soils. Only the furnace treatment significantly reduced cadmium uptake. Compared to the control soil, 51% and 40% of cadmium translocated in the 2% furnace slag and 5% red mud amended soils, respectively, whereas neither 5% red-mud nor furnace-slag treatments reduced cadmium uptake significantly (p>0.05).

Discussion

Application of specific amendments that can immobilize heavy metals in situ may provide a cost effective and feasible solution for the remediation of cadmium contaminated soils (Mench et al., 2000; Oste et al., 2002) [13].

It is clear from the previous studies that amendment treatment doesn’t change the total concentration of cadmium or even other heavy metals in soil but our study proved that application of amendment decrease the solubility and extractable fractions of cadmium heavy metals in soil. Decrease in concentration of soluble and extractable heavy metals in the amended soils can be characterized by significant increase in soil pH which is caused by the alkaline nature of amendments. Unlike other heavy metals, distilled water extractable cadmium concentration increased with Red-mud amendment. Dissolved organic carbon in soil significantly decreases the adsorption of cadmium onto soil surface by forming soluble organic complexes (Giusquiani et al., 1998) [8]. Some co-workers reported higher concentration of dissolved organic carbon in red-mud-amended soil and stabilization of cadmium adsorption by dissolved organic carbon (Gray et al., 2006) [9].

This study suggested that the increased pH caused by the alkaline nature of amendments led to a significant increase of metals associated with carbonated fractions. Moreover, red-mud and furnace slag, which are rich in Fe oxides can effectively binds with metal ions and results more metals to be associated with the Fe-Mn oxide fractions.

The reduced uptake of metals by mustard seedlings grown in amended soils is clearly related to the decrease of the phytoavailable of cadmium. Although soil amendments significantly reduce the uptake of cadmium in

mustard plants as well as the potential transfer of metals in the food chain, but this reduction is not sufficient to produce foodstuffs. So such soil shouldn't be recommended for agriculture purpose.
Various mechanism have been proposed to explain the reduced phytoavailability of cadmium in the amended soil but our study suggest that immobilization of heavy metal in this experiment is mainly because of increased soil pH due to alkaline nature of amendments that reduces heavy metal solubility in soil and increased cadmium adsorption on soil particles. Although red mud and furnace slag also contains large amount of Fe and Al oxides that results in their increased surface area and immobilized heavy metal in soil (Lombi et al., 2002) [12].

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