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Remediation of Contaminated Soil by Amendment of Nonhumus Soil with Humus-Rich Soil for Better Metal Immobilization

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Among various soil contaminants in polluted sites, heavy metals are of great concern because of their increasing abundance in the hydrological cycle and their relative high toxicity even at low concentrations and cumulative effects. Industries causing severe contamination of soils are the non ferrous metallurgical industry and pyrometallurgical processes (Adriano 2001). Soils are generally receiving large amounts of trace metals discharged into the aquatic ecosystem also by industrial activity (Nriagu and Pacyna 1988). Once released into the soil matrix, heavy metals have a potential impact on environmental quality and on human health through ground water and surface water (Alloway 1991). Higher concentration of heavy metals in soil may render soils non productive because of phytotoxicity and may cause bioaccumulation of heavy metals in animals and ultimately even human exposure (Abdel-Sahab et al.1994).

The technique of *in situ* immobilization is more appealing and ecofriendly as compared to conventional excavation, treatment and disposal methods because it reduces the risk of worker exposure during remediation and is less expensive and less disruptive to ecosystems (Chen 1998; Chen et al. 2000). Immobilization also limits the solubility of contaminants contained in the soil and captures the species within the soil (Yukselen et al. 2000). Improving the engineering properties of the immobilized material employing mechanisms like macro/micro encapsulation, absorption, adsorption or precipitation enhances detoxification capability (LaGrega et al. 1994). Several studies have shown that amending heavy metal contaminated soil with naturally occurring or artificial additives such as lime, phosphate, zeolite, bentonite, clay, Fe/Mn oxides and organic matter effectively reduced the metal concentration in aqueous and soil solutions (Chen et al. 2000; Kuo and McNeal 1984; Fu et al.1991; Mench et al.1994; Rebeda and Lepp 1994; Phillips 1998).

Humus soil formed as a result of leaf litter decay was used in this study. It generally contains humic substances such as humic acid, fulvic acid and humin, which are natural polymeric structures consisting of aromatic rings and aliphatic chains with hydroxyl, carboxyl and amino functional groups, and both hydrophilic and lipophilic sites (Stevenson 1994). Humic substances, even in traces, influence soil properties and influence the environmental fate and biological effects of

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pollutants. They strongly bind metals, and serve to hold micronutrient ions in soil. Because of their acid base character, humic substances also serve as buffers in soil. Pandey et al (2003) reported the efficiency of humic acid-entrapped calcium alginate beads in removing heavy metals. Singh and Oste (2001) reported that the metals were immobilized by organic matter and the immobilization effect depended on soil reaction and the kind of mineral species present in soils.

The purpose of the present study was to investigate the leachability of heavy metals from the soil fertified with a heavy metal solution and to compare the immobilization efficiency of humus soil used in combination with non-humus soil at different ratios.

MATERIALS AND METHODS

In the present study, humus and non-humus soils collected from orchard and non-orchard areas of Gheru campus of ITRC were used for the preparation of soil matrix. The background level of the metals in non-humus/humus soils were Cd (0.09/0.15), Cr (1.9/1.98), Cu (0.87/1.3), Fe (335/356), Mn (23.2/24.4), Ni (2.1/2.5), Pb (2.0/3.1), Zn (3.2/4.3) μg/g of soil respectively. Humus soil was mixed with non-humus soil to make the technology more cost effective. The soil samples collected were air dried, ground and sieved to remove unwanted material if any. Other chemicals used in the study were from E.Merck and AnalaR grade.

Solutions of the metal salts $CdCl_2.H_2O$, $CuCl_2.2H_2O$, $ZnSO_4.7H_2O$, $(CH_3COO)_2Pb.3H_2O$, $NiSO_4.7H_2O$, $MnCl_2.4H_2O$, $FeCl_3$ (anhydrous), $CrCl_3.6H_2O$ were prepared in deionized water in such a way to obtain 20 ppm of metal concentration in each case. The pH of the metal solution ranged from 6.28 to 7.54.

The cation exchange capacity of humus and non-humus soil was estimated by the method of Hesse (1971). For molecular radii and molecular surface areas of humic molecules, the method of Aiken (1984) was employed.

Forty g soil samples were prepared by mixing non-humus and humus soil in the ratio of 1:0, 0:1, 1:1, 1:2, 1:3, 1:4, 2:1, 3:1 in a horizontal shaft mixer. Prior to contamination of soil, the metals present in the non-humus and humus soils and in different combinations were estimated as base line data on ICP-AES (Inductively coupled plasma atomic emission spectroscopy) Labtam Plasma Lab 8440. One 100 ml H_2O containing 20 ppm metal mixture was spiked on these soils. The soil was dried and homogeneously mixed. The metals were again estimated in the contaminated soil. The background level of metals in non-humus/humus soils were subtracted to get the metal adsorbed on the soil.

A 10% leachate of the soil used in different combinations was prepared by adding 100 ml of deionized water to 10 g of soil sample in a Borosil conical flask and placed in a incubator adjusted to 25±1°C for 24 h with frequent mechanical stirring. It was then centrifuged at 11,000 g for 10 min and the supernatant was separated for TOC estimation. For total organic carbon, Shimadzu TOC 5000A model (Japan) was used, to measure total carbon (TC), inorganic carbon (IC) and total organic carbon (TOC) in water, by the combustion/non-dispersive infrared gas analysis method.

The soil matrix thus prepared was packed on a glass column of size 30x2.5 cm up to the height of 11 cm. One 100 ml of distilled water is passed through these columns under room temperature, pressure and gravity at the rate of 5 ml/h and the total fractions in each case were collected for leachability studies. The pH of the collected fractions was measured and metal content estimated after wet ashing.

RESULTS AND DISCUSSION

The cation exchange capacity (CEC) of non-humus and humus soil, molecular radius and molecular surface area of humic molecules are shown in Table 1. The three fold increase in the value of cation exchange capacity of humus soil as compared to non-humus soil indicate formation of insoluble metal organic complexes. The pH of collected effluent fraction was towards alkaline side. It ranged from 7.04 to 7.40 but it was highest being when the NHS:HS (1:3) ratio (Table 2).

Table 1. Cation exchange capacity of non-humus and humus soil, molecular radius and molecular surface area of humic molecules.

Parameters	Value
Cation exchange capacity (CEC) of non-humus soil in meq/100 g soil	14.72
Cation exchange capacity (CEC) of humus soil in meq/100 g soil	44.32
Molecular radius in mm	101.47
Molecular surface area (MSA) in cm^2	1293.19

Table 2. pH in the collected fractions after passing water through soil matrix and total organic carbon content (TOC) in 10% leachate prepared from soil matrix.

Soil matrix	pH of eluant water	10% leachate TOC (ppm
Non-humus soil (NH)	7.04	12.47
Humus soil (HS)	7.11	82.67
NHS:HS (1:1)	7.32	63.53
NHS:HS (1:2)	7.32	73.20
NHS:HS (1:3)	7.40	77.98
NHS:HS (1:4)	7.32	76.10
NHS:HS (2:1)	7.31	47.37
NHS:HS (3:1)	7.32	35.25

TOC in 10% leachate of soil increased with higher proportion of humus soil (Table 2). The concentrations of metal immobilized on the soil matrix and leached out in the collected fraction after passing the water through contaminated soil packed in a column are shown in Table 3 and 4. Of the various combinations tried, the combination non-humus and humus soil (1:3) was found to be most effective in metal immobilization. Out of 8 metals spiked on the soil Pb showed the maximum immobilization and Mn, the minimum. The immobilization trend was: Pb (69.5%), Cu (67.5%), Cr (66%), Ni (65%), Cd (64%), Fe (63%), Zn (62.25%), Mn (62%).

The process of immobilization depends on the nature, concentration and physicochemical state of pollutants present and specific characteristics of soil sites (Singh and Oste, 2001). The potential toxicity of metals in the surrounding

Table 3. Concentration of Cd, Cr, Cu and Fe immobilized on the soil matrix and leached out in the collected fraction after passing the water through contaminated soil (metal solution spiked soil) packed in column in different amendment ratios.

Soil matrix	Cd		Cr		Cu		Fe	
Soil amendment ratio	Conc. of metal immobilized (µg/g)	Conc. of metal leached (µg/ml)	Conc. of metal immobilized (µg/g)	Conc. of metal leached (µg/ml)	Conc. of metal immobilized (µg/g)	Conc. of Metal leached (µg/ml)	Conc. of metal immobilized (µg/g)	Conc. of metal leached (µg/ml)
Non-humus soil (NHS) 40 g	20.5	11.3	19.75	11.80	21.1	11.25	19.0	11.6
Humus soil (HS) 40 g	23.7	9.8	22.5	10.1	24.2	9.5	20.6	11.2
NHS:HS (1:1)	25.7	9.3	25.2	8.80	27.3	8.25	23.8	9.8
NHS:HS (1:2)	28.6	7.9	28.0	8.12	29.2	7.79	24.0	10.0
NHS:HS (1:3)	32.0	6.9	33.0	6.5	33.7	6.2	31.5	6.8
NHS:HS (1:4)	28.0	8.4	23.7	8.7	27.0	8.4	26.2	8.2
NHS:HS (2:1)	24.0	9.8	23.7	9.7	23.7	9.3	23.2	10.1
NHS:HS (3:1)	19.0	11.6	18.0	11.2	17.5	11.8	19.5	10.9

Note: 1. Values are presented as arithmetic means of three replicates.
2. Values are presented after substracting the background level of the metals in non-humus/humus soil

Table 4. Concentration of Mn, Ni, Pb and Zn immobilized on the soil matrix and leached out in the collected fraction after passing the water through contaminated soil (metal solution spiked soil) packed in column in different amendment ratios.

Soil matrix	Mn		Ni		Pb		Zn	
Soil amendment ratio	Conc. of metal immobilized (µg/g)	Conc. of metal leached (µg/ml)	Conc. of metal immobilized (µg/g)	Conc. of metal leached (µg/ml)	Conc. of metal immobilized (µg/g)	Conc. of Metal leached (µg/ml)	Conc. of metal immobilized (µg/g)	Conc. of metal leached (µg/ml)
Non-humus soil (NHS) 40 g	19.7	11.1	21.3	11.3	22.5	10.6	19.0	11.97
Humus soil (HS) 40 g	23.7	9.25	23.7	10.1	25.5	9.0	21.8	10.56
NHS:HS (1:1)	24.3	9.0	26.9	8.9	27.0	8.70	23.1	10.32
NHS:HS (1:2)	29.8	7.78	28.2	7.8	28.7	7.9	25.6	9.50
NHS:HS (1:3)	31.0	6.8	32.5	6.2	34.7	5.5	31.1	7.35
NHS:HS (1:4)	25.2	8.6	25.0	8.7	26.0	8.5	25.0	9.5
NHS:HS (2:1)	21.5	9.4	21.8	9.8	24.5	9.6	20.0	11.63
NHS:HS (3:1)	19.4	10.6	23.9	10.8	20.5	9.9	16.8	13.10

Note: 1. Values are presented as arithmetic means of three replicates.
2. Values are presented after substracting the background level of the metals in non-humus/humus soil

environment, either added as pollutants or naturally occurring, depends on their total concentrations in the soil, soil solution, and exchangeable forms. Basically, there are four major bonding mechanisms to describe a metal or metal compound bonded to soil system:

- i) physical sorption or precipitation of discrete metal, i.e. zerovalent, to soil constituents;
- ii) bonding of metal ions with organic matter;
- iii) chemosorption of metal oxide to fine grinded particles, such as SiO_2, kaolin etc. and
- iv) chemical dissolution into soil minerals through lattice diffusion.

The chemical behaviour of metals is primarily governed by retention and release reactions of solute with the soil matrix. The immobilization of Pb, Cu, Cr, Ni, Cd, Fe, Zn and Mn on the non-humus:humus soil matrix could be due to ability/tendency of humus soil to form stable complexes with metal ions, which in turn is attributed to the high content of total organic carbon, o-containing functional groups including –COOH, phenolic, alcoholic, enolic OH and ketonic C=O structures. The complexation site may be slightly different for different metals. The maximum immobilization in case of Pb and minimum in case of Mn in our study could be due to the affinity of humus soil toward different metals. The value of pH towards alkaline side as shown in our observation may also be one of the important factors for immobilization of these metals. McBride (1989) reported that the sorption behaviour of Zn, Cu and Cd in soils varies from soil to soil and is influenced by soil properties, such as pH, organic matter, clay and amorphous hydroxide contents, and cation exchange capacity. He further reported that a rise in pH generally decreases the mobility of heavy metals as many of the products used for immobilization of heavy metals in contaminated soils are alkaline materials. Further, the adsorption behaviour of heavy metals is greatly dependent on pH of solution and Pb is adsorbed on clay surfaces at pH value greater than 6 (EPA 1992). The idea of treating the heavy metal contaminated soils with phosphate has recently shown good promise and has been proposed an alternative to soil removal (Ma et al.1995). The findings suggest the potential utility of humus soil in minimizing the environmental risks of heavy metals from contaminated site through immobilization. Therefore, detailed studies under field conditions in the present time, with different soil pH and humus content, will help in the optimization of the use of soil humus, in rehabilitating toxic metal contaminated soils.

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