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Immobilization of Heavy Metals in Contaminated Soil Using Nonhumus–Humus Soil and Hydroxyapatite

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Contamination of soil by the release of heavy metals as a result of industrial and anthropogenic activities is a threat to human health and ecosystem. Non-ferrous metallurgical Industries and pyrometallurgical processes are the main source for causing severe contamination of soils (Adriano, 2001).Soils are generally receiving large amounts of trace metals discharged into the aquatic ecosystem also by industrial activity (Nriagu and Pacyna,1988).Presence of heavy metals in soils are known to have potential impact on environmental quality and on human health via ground water and surface water (Kim et al. 1997). Moreover, concentrations of heavy metals in soil may render soils nonproductive because of phytotoxicity and may cause bioaccumulation of heavy metals in animals and human exposure (Abdel-Sahab et al. 1994).

The technological solutions for treatment of contaminated sites are usually costly and many a times not practically feasible, especially in developing countries. Among the various techniques employed earlier, the technique of *in situ* immobilization could be an environmentally sustainable and cause effective alternative for the remediation of polluted soils. It reduces the risk of worker exposure during remediation and is less expensive and less disruptive to ecosystems (Dermatas,1994; Chen et al.2000). It also limits the solubility of contaminants contained in the soil and capture the species within the soil (Yukselen et al.2000).Chemical remediation techniques have been used to immobilize heavy metals in the contaminated soils and to reduce the soluble concentrations of trace elements in soils by the process of precipitation, adsorption or complexing with organic matter (Mench et al.1994).Increasing the soil pH by liming resulted in immobilization of several metals (Cd, Cu, Ni, Zn) and reduced their bioavailability by many folds (Hooda and Alloway, 1996).

Humus soil formed as a result of leaf litter decay was used in this study. Among the humic substances, humic acids are natural organic macromolecules with multiple properties and high structural complexity and behave as supramolecules, which are able to polymerize, aggregate, form micelles and might also form supramolecular ensembles with other compounds (Steed and Atwood, 2000). Humic substances even in traces influence soil properties and influence the environmental fate and biological effects of pollutants. Misra and Pandey (2004)

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used non humus soil with humus rich soil for better metal immobilization.The idea of treating the heavy metal contaminated soils with phosphate has recently shown good promise and has been proposed as an alternative to soil removal (Berti and Cunningham, 1997). Apatite minerals are known to react with many transition and heavy metals and metalloids to rapidly form secondary phosphate precipitates that are stable over a wide range of geochemical conditions (Wright, 1990). Several studies have shown that treatment of hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$], phosphate rock or phosphoric acid to contaminated waters and soil effectively reduced lead contamination in aqueous and soil solutions and resulted in formation of pyromorphite, a compound characterized by very low solubility (Ma et al. 1994; Seaman et al. 2001). The purpose of the present study was to investigate the leachability of heavy metals from the soil fortified with heavy metal solution and to compare the immobilization efficiency of various concentrations of hydroxyapatite used in combination with non-humus: humus soil in the ratio of 1:3.

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 soil respectively. The cation exchange capacity of non-humus and humus soil determined by the method of Hesse (1971) were 14.72 and 44.32 meq/100 g soil respectively. The soil samples collected were air dried, ground and sieved to remove unwanted material if any.

Hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$] obtained from Aldrich chemical Company Inc., Milwaukee, USA was used as a metal immobilizing additive. 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 µg/ml of metal concentration in each case. The pH of the metal solution ranged from 6.28 to 7.54.

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 determined for the background level of metals with ICP-AES (Inductively coupled plasma atomic emission spectroscopy) Labtam Plasma Lab 8440. One 100 ml water containing the desired metallic salt solution (20 µg/ml) metal mixture was poured on these soils. The soil was dried and homogenously mixed.

Separate glass column of size 30x2.5 cm each were packed with heavy metals contaminated soil mixed in different ratios. 100 ml deionized water was passed through these columns and in the flow through, the concentrations of metals leached were measured. The soil matrix prepared in the ratio of non-humus, humus soil (1:3) combination gave optimal results. The performance of soil matrix containing higher concentrations of humus soil were not satisfactory. The background level of metals in non-humus/humus soils were substracted to get the metal adsorbed on the soil. For immobilization of metals due to hydroxyapatite (a metal immobilizing additive), the non-humus: humus soil prepared in the ratio of 1:3 was mixed with 0.5 , 1.0 and 5% hydroxapatite w/w basis in a plastic flask containers by rotation. 100 ml of water containing 20 μg/ml of metal mixture was then poured on these non-humus:humus: hydroxyapatite matrix.

For leachability study, the matrix prepared above was packed in the glass columns of size 30 x 2.5 cm upto a height of 11.0 cm separately. 100 ml of distilled water is passed through these columns under room temperature, pressure and gravity at a rate of 5 ml/h. The pH of the collected fractions was measured and metal content estimated after wet washing. From the leachability study, the concentration of metals immobilized were calculated.

To find out the percent of immobilization, the total amount applied, the amount net adsorbed and passed down and the total and leached out were estimated and what is left behind is taken as immobilized.

RESULTS AND DISCUSSION

The pH of collected fraction after passing water through columns containing different soil matrix and total organic carbon in 10% leachate of soil matrix are shown in Table 1. Increase in the pH from 7.4 to 8.0 was noticed after the addition of hydroxyapatite. The value of total organic carbon in the leachate of humus soil was found to be maximum (82.67 ppm). The addition of hydroxyapatite did not show any effect.

Table 1. pH in the collected fractions after passing water through soil matrix and TOC in 10% leachate of soil matrix.

Soil matrix	pH of eluant water	TOC in 10% leachate (ppm)
Non-humus soil (NHS)	7.04	12.47
Humus soil (HS)	7.11	82.67
NHS:HS (1:3)	7.40	77.98
NHS:HS (1:3) + 0.5% hydroxyapatite	7.60	78.20
NHS:HS (1:3) + 1% hydroxyapatite	7.80	78.25
NHS:HS (1:3) + 5% hydroxyapatite	8.00	78.25

The concentrations of metal immobilized on different soil matrix packed in column (non-humus/ humus and hydroxyapatite) and leached out in the collected fraction after passing the water are shown in Table 2 and 3. Of the various combinations tried, the combination non-humus and humus soil (1:3) was found to be most effective. Out of 8 metals fortified with this combination of soil, Pb showed the maximum (69.5%) immobilization and Mn, the minimum (62%). With the increase in the concentration of hydroxyapatite in soil from 0.5% to 5%, there was progressive increase in the concentration of metals, immobilized and progressive decrease in concentration of metals leached.The immobilization rates of metal in soil matrix was Pb (92.8%) > Cu (91.2%) > Cr (90.4%) > Cd (88.2%) > Fe (78.6%) > Ni (75.8%) > Zn (75.2%) > Mn

(74.8%) and leachability rates of metal from soil matrix was Mn (20.5%) > Zn (18.5%) > Ni (17.5%) > Fe (6.5%) > Cd (6.0%) > Cr (5.5%) > Cu (4.5%) > Pb (3%).

In situ strategies for remediation of metals frequently involve minimizing the mobility of contaminants by transferring them to non labile phases via chemically or biologically induced transformations. Immobilization depends on the nature, concentration and physicochemical state of metals, their speciation, solubility, specific characteristics of soil sites and nature of additives (Rulkens et al. 1998).

Table 2. Concentration of Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn immobilized on the soil matrix packed in column.

Soil matrix	Concentration of metal immobilized in µg/g							
	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Non-humus soil (NHS) 40 g	20.5	19.75	21.1	19.0	19.7	21.3	22.5	19.0
Humus soil (HS) 40 g	23.7	22.5	24.2	20.6	23.7	23.7	25.5	21.8
NHS:HS (1:3) (10+30) g	32.0	33.0	33.7	31.5	31.0	32.5	34.7	31.1
NHS:HS (1:3) (10+30) g + 0.5% hydroxyapatite	39.0	41.5	41.6	37.0	33.9	33.0	44.2	35.5
NHS:HS (1:3) (10+30) g + 1% hydroxyapatite	41.2	42.3	42.1	38.5	35.3	36.2	46.0	37.0
NHS:HS (1:3) (10+30) g + 5% hydroxyapatite	44.1	45.2	45.6	39.3	37.4	37.9	46.4	37.6

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.

The immobilization of Pb, Cu, Cr, Ni, Cd, Fe, Zn and Mn on the non-humus:humus soil (1:3) matrix and in the presence of hydroxyapatite in our study could be due to (i) the formation of stable complexes between –COOH, phenolic, alcoholic, enolic OH and ketonic C=O structures present on the humus soil surface and metal ions and (ii) ion exchange processes at the surface of humus soil due to high cation exchange capacity and hydroxyapatite or substitution of calcium in hydroxyapatite by other metals. The variation in immobilization of metal depends upon the complexation sites, affinity of soil matrix and ionic radii of different metals.

The ionic radius of Ca^{2+} (1.14 A°) is closer to one of Cd^{2+} (1.09 A°) than the radius of Zn^{2+} (0.88 A°), Cu^{2+} (0.87 A°), Mn^{2+} (0.80 A°) and Ni^{2+} (0.72 A°). So that isomorphic substitution of Ca^{2+} by Cd^{2+} is more favorable. The isomorphic substitution by other metals would be less favorable. Ma et al (1994) reported the removal of Pb through dissolution of hydroxyapatite followed by precipitation as hydroxypyromorphite.

$$Ca_{10}(PO_4)(OH)_{2(s)} + 14H^+ (aq) \xleftrightarrow{\text{dissolution}} 10Ca^{2+} (aq) + 6H_2PO_4^- (aq) + 2H_2O \text{ --(1)}$$

$$10Pb^{2+} (aq) + 6H_2PO_4^- (aq) + 2H_2O \xleftrightarrow{\text{precipitation}} Pb_{10} (PO_4)_6(OH)_{2(s)} + 14H^+ (aq)\text{---(2)}$$

Table 3. Concentration of Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn leached in the collected fraction after passing the water through the soil matrix containing metals.

Soil matrix	Concentration of metal immobilized in μg/g							
	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Non-humus soil (NHS) 40 g	11.3	11.80	11.25	11.6	11.1	11.3	10.6	11.97
Humus soil (HS) 40 g	9.8	10.1	9.5	11.2	9.25	10.1	9.0	10.56
NHS:HS (1:3) (10+30) g`	6.9	6.5	6.2	6.8	6.8	6.2	5.5	7.35
NHS:HS (1:3) (10+30) g + 0.5% hydroxyapatite	2.4	1.7	1.9	2.9	5.2	5.1	1.6	4.5
NHS:HS (1:3) (10+30) g + 1% hydroxyapatite	1.8	1.2	1.4	1.9	4.8	4.4	1.2	3.8
NHS:HS (1:3) (10+30) g + 5% hydroxyapatite	1.2	1.1	0.9	1.3	4.1	3.5	0.6	3.7

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.

According to Shashkova et al. (1999) lead would be adsorbed first on the surface of the apatite particle, then, by diffusion, cation exchange would take place between apatite Ca^{2+} ions and Pb^{2+} ions in solution. Several workers have observed that zinc and cadmium also may form insoluble phosphate complexes, although not to the same extent as lead (Cao et al. 2003). McGowen et al. (2001) reported that diammonium phosphate treatment increased retardation 2 fold for Cd, 6 fold for Zn, and 3.5 fold for lead. Apart from this pH is another factor which influence the immobilization processes. The addition of hydroxyapatite in our study leads to a strong pH increase. Immobilization through the process of ion exchange and surface complexation will increase when pH increases concerning the precipitation of hydropyromorphite. It was shown that at a given lead and phosphate concentration, more hydropyromorphite was formed at pH 5.0 than pH 6.0 or 7.0 (Laperche et al. 1996). Also, the increase in Pb immobilization is expected due to negative charge present on clay particle and pH value greater than 6 (Dermatas, 1994). In the present study, the potential utility of humus rich soil along with hydroxyapatite in minimizing the environmental risks of heavy metals from contaminated site through immobilization is highlighted. The findings suggest that amending the non-humus soil with humus soil and hydroxyapatite can immobilize toxic metals more effectively and also reduce their bioavailability.

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