

Selectivity sequences and sorption capacities of phosphatic clay and humus rich soil towards the heavy metals present in zinc mine tailing

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Abstract

Sorption efficacy of phosphatic clay and humus rich soil alone and on combination were tested towards heavy metals present in zinc mine tailing (Zawar Zinc Mine), Udaipur (India). Characterization of the zinc mine tailing sample indicated the presence of Pb, Cu, Zn and Mn in the concentration of 637, 186, 720 and 577 $\mu\text{g g}^{-1}$, respectively. For sorption efficacy, the zinc mine tailing soil were properly amended with phosphatic clay and humus rich soil separately and in combination and leachability study was performed by batch experiment at different pH range from 3 to 9. The data showed that the percent leachability of heavy metal in non-amended soil was 75–90%. After amendment with phosphatic clay percent leachability of heavy metals became 35–45%. Further, the addition of humus soil to phosphatic clay decreased the percent leachability up to 5–15% at all tested pH. Column leachability experiment was performed to evaluate the rate of leachability. The shape of cumulative curves of Pb, Cu, Zn and Mn showed an increase in its concavity in following order: $\text{Pb} < \text{Cu} < \text{Zn} < \text{Mn}$. The most common selectivity sequence calculated on the basis of distribution coefficient (K_d) from the batch experiment was $\text{Pb} > \text{Cu} > \text{Zn} > \text{Mn}$. Further, Langmuir isotherms applied for the sorption studies indicated that phosphatic clay in the presence of humus soil had high affinity for Pb followed by Cu, Zn and Mn, with sorption capacities (b) 139.94, 97.02, 83.32 and 67.58 $\mu\text{g g}^{-1}$, respectively.

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1. Introduction

Contamination of soil by heavy metals, mainly due to acid mine drainage, tailings embankments, mining rock dumps and metallurgical waste piles pose a serious threat to the environment [1]. These heavy metals may adversely affect the soil ecology, agricultural productivity, food chain and water quality [2]. There are reports that even a low concentration of heavy metals in the soil are known to have potential impact on environmental quality and human health via ground water and surface water [3].

The metal mobility largely depends upon sorption and leachability of heavy metals with different soil constituents. In recent years, attention has been focused on the development of in situ immobilization methods that are generally less expensive and

disruptive to the natural landscape, hydrology and ecosystem than conventional excavation treatment and disposal methods [4,5]. The main goal of this technique is to reduce the fraction of toxic metals that is potentially mobile or by increasing retention of metals in the non-mobile solid phase.

Immobilization by means of soil amendments has been recently investigated as a valuable alternative technique for a wide range of contaminated sites [6]. Immobilization prevents the transfer of contaminants into deeper soil layers and into ground water. Several efforts have been made to use inexpensive soil amendments such as carbonates, phosphate rocks, alkaline agents, zeolites, clay minerals and organic materials as immobilizing agents for remediating metal contaminated soil [7–11]. These amendments can lead to immobilization of metals in a variety of ways. Firstly, some amendments dissolve supplying alkalinity to acid polluted soil causing the precipitation of insoluble phases such as metal-phosphate and carbonates or co-precipitated in the form of hydroxides [12,13]. Secondly, the increase in alkalinity promotes the metal sorption via surface

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complexation processes [14,15]. Among these, phosphatic clay possesses a high potential to sorb the heavy metal, because it has a high content of apatite mineral $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH}, \text{F}, \text{Cl})_2$ up to 24–34% of the total dry weight [16]. The other immobilizing agent is humic substance formed as a result of leaf litter and decay. These humic substances are reported to strongly influence the fate of metal ion owing to their different functional groups at different proportion and configuration and potentially impact on the remediation of soil polluted with heavy metal [17–19].

The mobility and the fate of metals in soils can be related to their distribution between the solid and solution phases [20] and thus, to their distribution coefficient (K_d) [21,22]. According to Alloway [23], K_d is a useful parameter for comparing the sorptive capacities of the different soil or materials for a specific ion under identical experimental conditions. Another important properties governing the mobility and fate of metals in soil and aqueous phases are surface area, surface charge, pH, ionic strength and concentration of complexing ligands [24].

Most of the studies on heavy metal sorption are focused on single adsorbent, which may not be efficient for all the metals and also may not be cost effective when used for in situ immobilization. In the present investigation, the soil obtained from zinc mine tailing were amended with two soil (phosphatic clay and humus rich soil) and sorption and leachability of heavy metals at different pH were studied to test the capacities of these soil for better immobilization.

2. Materials and method

2.1. Sampling and characterization of the zinc mine tailing soil, phosphatic clay and humus soil

The surface soil sample of zinc mine tailing was collected from Zawar Zinc Mine Udaipur (India). For amendment, the humus rich soil was collected from ITRC Gheru Campus and phosphatic clay from phosphate rock mining area, Udaipur (India). The collected soil samples were air dried, ground and passed through 60-mesh sieve to remove unwanted material if any.

For determination of the soil pH and dissolved organic carbon, 1.0 g of each soil sample were dissolved in 30.0 ml deionized water. A continuous and vigorous shaking was performed for 24 h at room temperature. The slurries were centrifuged at $3000 \times g$ for 30 min and supernatants were separated. In the supernatant, the pH was determined by pH meter and total organic carbon by total organic carbon analyzer (TOC-5000A Shimadzu, Japan). Cation exchange capacity of each soil was determined by the method of Hesse [25]. For metal analysis, 1.0 g of each soil was digested in the microwave digestion system (Anton Paar Multiwave 3000). The voltage, pressure and time required for the complete digestion were standardized for each sample. Acid mixture used for digestion was $\text{HNO}_3:\text{HClO}_4$ (3:1, v/v). After complete digestion, the metals were analyzed by the ICP-AES using the method of APHA [26]. The values of these parameters are given in Table 1.

Table 1
Characterization of zinc mine soil, phosphatic clay and humus soil

Parameters	Zinc mine tailing	Phosphatic clay	Humus soil
pH	7.96	6.75	7.45
CEC (mequiv./100 g soil)	24.48	45.92	62.58
Dissolved organic carbon ($\mu\text{g ml}^{-1}$)	16.85	34.85	82.67
Background metal concentration ($\mu\text{g g}^{-1}$)			
Pb	673.51	9.68	7.94
Cd	1.52	ND	ND
Mn	577.68	18.25	22.93
Co	4.12	5.31	1.52
Cr	1.16	8.77	7.14
Cu	186.23	2.28	1.15
Ni	9.67	11.57	2.87
Zn	720.54	4.21	1.13

2.2. Amendment of the zinc mine tailing soil

For suitable amendment, the mine soil was mixed with phosphatic clay and humus soil in the following ratio and four sets were prepared. The first set contained the zinc mine tailing soil (ZMTS), which served as control, the second set, ZMTS and phosphatic clay (PC) in the ratio of 1:1 (w/w). The third set, ZMTS and humus rich soil (HS) in the ratio of 1:1 (w/w) and the fourth, ZMTS and mixture of PC and HS in the ratio of (2:1:1) (w/w/w). For proper amendment, the soils were incubated at 60% water holding capacity (WHC) for 2 days at room temperature.

2.3. Leachability study

For leachability, both batch and column studies were performed. For batch equilibrium study, the extracting solutions were prepared at different pH (3–9). The acidic solutions were prepared from the glacial acetic acid and basic solutions from the sodium hydroxide. One gram of each soil sample was taken in the centrifuge tube with 30.0 ml of different varying pH extracting solution. A continuous and vigorous shaking was performed for 24 h at room temperature. The slurries were centrifuged at $5000 \times g$ for 30 min and supernatants were separated. The supernatants were subjected to metal analysis by ICP-AES using the above method. For column study, separate glass columns of size 3 cm \times 15 cm with a sintered glass filter at the bottom was packed with 100 g of each soil sample. These columns were leached with 400 ml (approx. 560 mm annual rainfall in the mining area) of deionized water under constant flow and 100 ml of each fraction were collected. The concentrations of metal leached were measured. The percent leachability of heavy metals from the soil is calculated by following equation:

Percent leachability

$$= \frac{\text{concentration of metal leached per 100 ml}}{\text{total amount of metal present in contaminated soil}} \times 100$$

All experiments run in triplicate.

2.4. Sorption experiment

To evaluate the feasibility of the amendment, batch sorption experiments were performed. Aqueous stock solution of $200 \mu\text{g l}^{-1}$ of Pb^{2+} , Cu^{2+} , Zn^{2+} and Mn^{2+} were prepared by dissolving nitrate salt of each metal in water containing 0.05 M KNO_3 as background electrolyte. Different metal concentration solutions ranging from 0 to $200 \mu\text{g l}^{-1}$ with the increment of $20 \mu\text{g l}^{-1}$ were prepared from the solution with the help of deionized distilled water. One gram of phosphatic clay amended with humus soil was added into 30.0 ml of each metal solution having different concentration. The centrifuge tubes were shaken properly at room temperature for 48 h . The slurries were centrifuged at $5000 \times g$ for 45 min and supernatants were separated. The supernatants were again subjected to metal analysis by ICP-AES using the above method. The amount of sorbed metal was

taken as the difference between the amounts added initially and that remaining in solution after equilibrium.

3. Results and discussion

Metal sorption onto heterogeneous material is largely controlled by the electrostatic interactions between ion and charge surface of these material [27].

3.1. Leachability study

3.1.1. Batch equilibrium

The percent leachability of heavy metals from the ZMTS and ZMTS amended with PC and HS at different pH is shown in Fig. 1a–d. The data showed that the percent leachability of heavy metal from ZMTS (control) was 75 – 90% . After amendment with

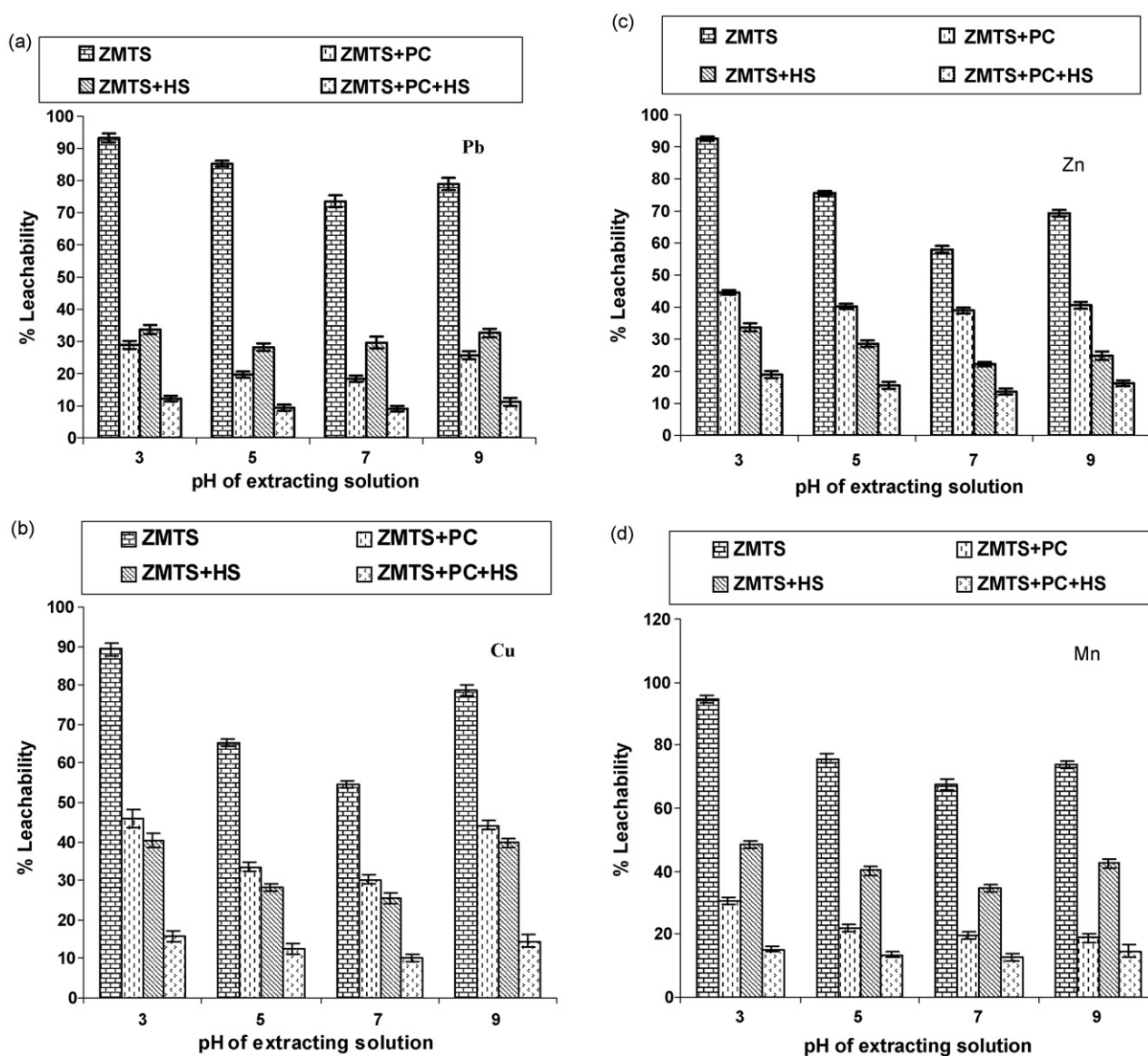


Fig. 1. (a) Percent leachability of Pb in different soil system as a function of pH ZMTS = zinc mine tailing soil, PC = phosphatic clay, HS = humus soil. (b) Percent leachability of Cu in different soil system as a function of pH ZMTS = zinc mine tailing soil, PC = phosphatic clay, HS = humus soil. (c) Percent leachability of Zn in different soil system as a function of pH ZMTS = zinc mine tailing soil, PC = phosphatic clay, HS = humus soil. (d) Percent leachability of Mn in different soil system as a function of pH ZMTS = zinc mine tailing soil, PC = phosphatic clay, HS = humus soil.

PC percent leachability of heavy metals became 40–45%. Further, the addition of HS to PC decreased the percent leachability up to 10–15%. PC showed greater immobilization towards Pb as compared to Zn, Cu and Mn at neutral to slightly acidic pH whereas addition of HS showed better immobilization results at all the pH tested. The reason for this could be the presence of organic matter in the humus soil. Qiao et al. [28] have studied the chemical speciation and extractability of Zn, Cu and Cd in two contrasting biosolids-amended clay soils and found that all the three heavy metals had different extractabilities and chemical speciation against different extractants. Vega et al. [29] have shown that heavy metal sorption depends upon the soil characteristics. Humic acids present in humus soil are found to enhance the metal adsorption capacity of mineral surfaces

through the formation of ternary mineral surface-metal-organic ligand complexes [30]. Brown et al. [31] reported that Cu and Pb are preferably associated to the soil organic fraction and they can form stable complexes with organic matter at lower pH. On the other hand Bradl [32] reported that Pb and Cu are the metals for which the organic matter presents greater affinity. He further reported that in addition to soil organic matter, the most important soil sorbents for Cu are Fe and Mn oxides. Luo and Christie [33] reported that Cu can be preferentially combined with organic matter while Zn appears to be more sensitive to soil acidity. Sauve et al. [34] demonstrated that iron oxide play an important role in Pb retention whereas other studies indicate that Mn oxides present more affinity for Pb absorption than other soil oxides [35]. The probable mechanism in the case of Pb is

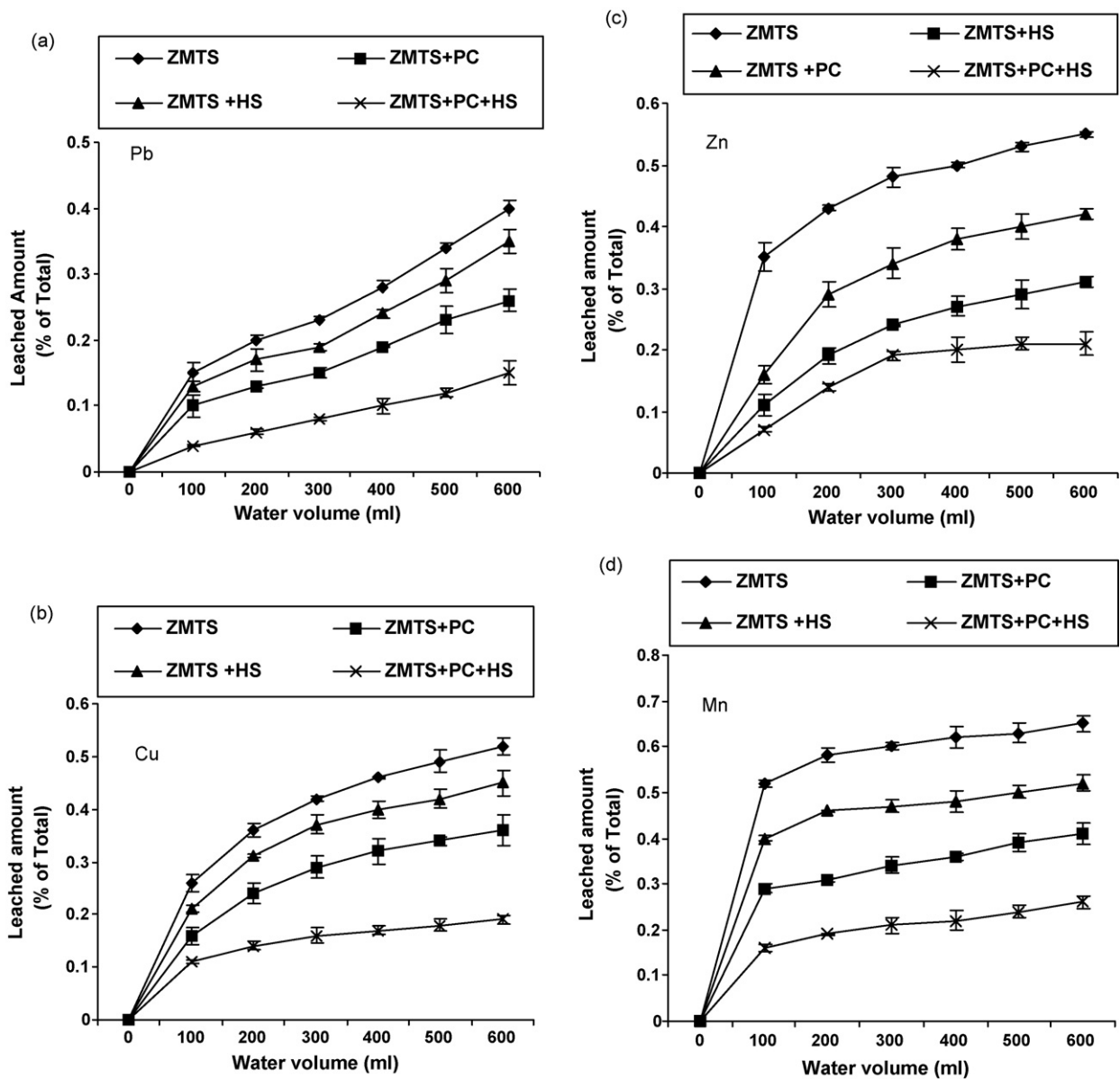


Fig. 2. (a) Cumulative curve of Pb leaching in different soil system ZMTS = zinc mine tailing soil, PC = phosphatic clay, HS = humus soil. (b) Cumulative curve of Cu leaching in different soil system ZMTS = zinc mine tailing soil, PC = phosphatic clay, HS = humus soil. (c) Cumulative curve of Zn leaching in different soil system ZMTS = zinc mine tailing soil, PC = phosphatic clay, HS = humus soil. (d) Cumulative curve of Mn leaching in different soil system ZMTS = zinc mine tailing soil, PC = phosphatic clay, HS = humus soil.

precipitation whereas for other metals it is surface complexation. The data showed the maximum retention of metal at pH 5 and 7. Addition of HS in PC increases more binding sites for the heavy metals at the surface of the soil, leading to increased immobilization at different pH range. It appears that both the PC and HS lose their protons at increasing pH and become negatively charged and causing electrostatic binding towards heavy metals. Heidmann et al. [36] found that addition of the fulvic acid to the clay strongly increased the metal sorption onto kaolinite at all studied pH. Enhancement of the metal sorption to kaolinite by fulvic acid was strongest at low pH similar to that reported here, where fulvic acid contributed to high affinity binding site of kaolinite.

3.1.2. Column leaching

The percolation curves of Pb, Cu, Zn and Mn (in the cumulative form) obtained from the ZMTS (control) and the soil amended with PC and HS alone and mixture are shown in Fig. 2a–d. The shape of the percolation curve is indicative of leaching rate of metals from the soil. It also reveals an increase in their concavities with a clear tendency to reach the ‘plateau’. The shape of percolation curve in the present study showed an increase in its concavity following the order $Pb < Cu < Zn < Mn$. These findings are in consistent with the findings of Alvarez-Ayuso and Garcia-Sanchez [37]. In the case of ZMTS, percentages of metal leached with respect to the total metal content present in ZMTS are 0.40% for Pb, 0.52% for Cu, 0.55% for Zn and 0.65% for Mn. Addition of PC in the ZMTS reduce the fraction to 0.26% for Pb, 0.36% for Cu, 0.42% for Zn and 0.52% for Mn. Addition of HS in PC further reduce the fraction to 0.15% for Pb, 0.21% for Cu, 0.19% for Zn and 0.36% for Mn. The results obtained in column leachability test are consistent with batch equilibrium test.

3.2. Distribution coefficient (K_d)

K_d is calculated for the purpose of ranking metals according to their extent of sorption. On the basis of K_d values it is possible to calculate the mobility and fate of competing metals in the soil [22].

The distribution coefficient (K_d) for each metal and soil were calculated by using the following equation:

$$K_d = \frac{\text{amount of metal adsorbed at equilibrium } (\mu\text{mol kg}^{-1})}{\text{concentration of metal in the solution at equilibrium } (\mu\text{mol l}^{-1})} \quad (1)$$

To establish the preference order of sorption of the metals by the different amendment, Kaplan et al. [38] used $K_d \sum$ values that are the sum of the sorbed surface species and sum of metallic aqueous species.

$$K_d \sum = \left(\frac{\sum C_{M_j,ads}}{\sum C_{j,M_j,aq}} \right) \quad (2)$$

where $\sum C_{M_j,ads}$ and $\sum C_{j,M_j,aq}$ are the concentration of metal j in soil ($\mu\text{g g}^{-1}$) and solution ($\mu\text{g l}^{-1}$), respectively. The

most common selectivity sequence calculated on the basis of distribution coefficient (K_d) from the batch experiment was $Pb > Cu > Zn > Mn$ (Table 3). According to Anderson and Christensen [39] high values of K_d indicate that metal is significantly sorbed or retained by solid phase through sorption reactions, while low values signify that an important proportion leached from soil. These selectivity sequences are depend on the tendency of the metals to form covalent bonds with sorbed surfaces by their ionic radii and ionization potentials and proposed a selective sequence of $Pb > Cd > Cu > Co > Ni > Zn$ [40]. According to McBride [41] the electronegativity is the determining factor of chemisorption. Based on this, he proposed the selectivity sequence: $Cu > Ni > Co > Pb > Cd > Zn > Mg > Sr$. He further suggested that if chemisorption of metals depend only on the electrostatic force of attraction, the strongest bond would be formed by the metal with the highest charge-to-radius ratio, giving rise to the sequence: $Ni > Mg > Cu > Co > Zn > Cd > Sr > Pb$. However, in our study, selectivity sequences did not exactly fol-

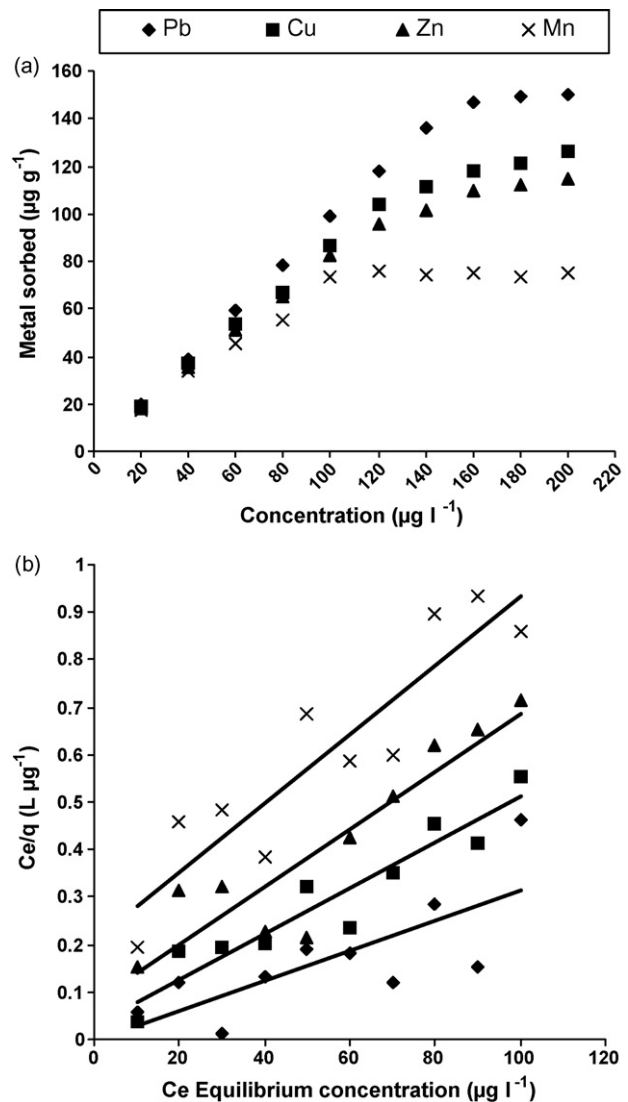


Fig. 3. (a) Sorption isotherms of Pb^{2+} , Cu^{2+} , Zn^{2+} and Mn^{2+} on the phosphatic clay amended with humus soil. (b) Linear fitting of sorption isotherms after using the linear Langmuir equation.

low the order of electronegativity of the metal cations i.e. Pb (1.8), Cu (1.9), Zn (1.6) and Mn (1.6). Gomes et al. [42] have evaluated the selectivity sequences and competitive adsorption of the heavy metals by Brazilian soils on the basis of K_d values. The most common sequences were $Cr > Pb > Cu > Cd > Zn > Ni$ and $Pb > Cr > Cu > Cd > Ni > Zn$. They are also of the opinion that sequences did not exactly follow the order of electronegativity of the metal cations.

3.3. Sorption isotherm

To evaluate the feasibility of sorption of heavy metal on the ZMTS amended with PC and HS in combination, the Langmuir model for the associated parameter on the above concentrations has been used (Fig. 3a). The Langmuir adsorption equation can be expressed as:

$$q_i = \frac{Kc_i b}{1 + Kc_i} \quad (3)$$

where q_i is the amount of metal sorbed by amended soil ($\mu\text{g g}^{-1}$), c_i the equilibrium concentration in ($\mu\text{g l}^{-1}$); K the Langmuir concentration ($1 \mu\text{g}^{-1}$) and b is the maximum sorption capacity ($\mu\text{g g}^{-1}$).

Rearranging Eq. (3) in linear form it becomes:

$$\frac{c_i}{q_i} = \frac{1}{Kb} + \frac{c_i}{b} \quad (4)$$

Plotting c_i/q_i versus c_i , the slope is $1/b$ and the intercept is $1/kb$. The sorption data were fit to a linear form of the Langmuir equation and are plotted in Fig. 3(b). Langmuir sorption parameters of amended soil for all the metals were calculated by using least square fitting method. The data showed that PC in the presence of HS had high affinity for Pb followed by Cu, Zn and Mn,

Table 2
Langmuir parameters for the sorption of heavy metals onto amended soil

Metals	b ($\mu\text{g g}^{-1}$)	k ($1 \mu\text{g}^{-1}$)	R^2
Pb	139.94	4.54	0.99
Cu	97.02	2.09	0.98
Zn	83.32	1.63	0.97
Mn	67.58	0.97	0.89

with sorption capacities 139.94, 97.02, 83.32 and 67.58 $\mu\text{g g}^{-1}$, respectively. Sorption parameter for amended soil showed variation among the metals (Table 2). Results showed that maximum sorption capacity (b) for amended soil remained highest for Pb as compared to Cu, Zn and Mn. The sorption isotherm also showed the immobilization of metals on the amended soil in the order of $Pb > Cu > Zn > Mn$. The essential characteristic of Langmuir isotherm is its dimensionless constant separation factor R_L , which is defined by McKay et al. [43]. The R_L factor can be defined as the following equation:

$$R_L = \frac{1}{1 + bC_0} \quad (5)$$

where b is the Langmuir constant, C_0 the initial concentration and R_L indicates the shape of isotherm ($R_L > 1$ unfavourable; $R_L = 1$ linear; $0 < R_L < 1$ favourable and $R_L < 0$ irreversible). The values of R_L were found to be less than 1 and greater than 0 indicating the favourable sorption of heavy metals on PC and HS.

Ma et al. [10] proposed the Pb retention by hydroxyapatite is controlled by the metal dissolution, followed by the hydroxypyromorphite $[\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2]$ precipitation. Cao et al. [44] reported that phosphate induced formation of fluoropyromorphite $[\text{Pb}_{10}(\text{PO}_4)_6(\text{F})_2]$ is primarily responsible for Pb immobilization by phosphatic rock whereas Cu and Zn reten-

Table 3
Distribution coefficients (K_d) and selectivity sequences

pH	Soil system	K_d (1 kg^{-1})				Selectivity sequences
		Pb	Cu	Zn	Mn	
3	ZMTS	0.460 ± 0.023	0.419 ± 0.056	0.409 ± 0.056	0.967 ± 0.052	Mn > Pb > Cu > Zn
	ZMTS + PC	4.528 ± 0.048	2.346 ± 0.081	1.956 ± 0.076	1.203 ± 0.065	Pb > Cu > Zn > Mn
	ZMTS + HS	1.985 ± 0.056	5.454 ± 0.070	2.281 ± 0.052	1.439 ± 0.08	Cu > Zn > Pb > Mn
	ZMTS + (PC + HS)	11.288 ± 0.055	6.407 ± 0.054	6.351 ± 0.062	5.288 ± 0.12	Pb > Cu > Zn > Mn
5	ZMTS	0.916 ± 0.071	0.522 ± 0.086	0.589 ± 0.067	1.024 ± 0.12	Mn > Pb > Zn > Cu
	ZMTS + PC	6.676 ± 0.13	4.478 ± 0.22	3.054 ± 0.14	1.318 ± 0.18	Pb > Cu > Zn > Mn
	ZMTS + HS	3.676 ± 0.12	6.416 ± 0.24	5.531 ± 0.35	2.226 ± 0.11	Cu > Zn > Pb > Mn
	ZMTS + (PC + HS)	25.238 ± 0.58	18.484 ± 0.29	17.624 ± 0.32	12.551 ± 0.35	Pb > Cu > Zn > Mn
7	ZMTS	1.117 ± 0.089	0.840 ± 0.089	0.803 ± 0.074	1.483 ± 0.29	Mn > Pb > Cu > Zn
	ZMTS + PC	4.832 ± 0.17	4.087 ± 0.19	2.597 ± 0.39	1.276 ± 0.22	Pb > Cu > Zn > Mn
	ZMTS + HS	3.906 ± 0.32	7.842 ± 0.11	6.310 ± 0.25	1.846 ± 0.25	Cu > Zn > Pb > Mn
	ZMTS + (PC + HS)	40.546 ± 0.35	36.223 ± 0.18	30.162 ± 0.26	26.238 ± 0.35	Pb > Cu > Zn > Mn
9	ZMTS	1.180 ± 0.055	0.860 ± 0.086	0.726 ± 0.023	1.192 ± 0.048	Mn > Pb > Cu > Zn
	ZMTS + PC	5.906 ± 0.08	3.637 ± 0.13	3.840 ± 0.14	1.254 ± 0.089	Pb > Zn > Cu > Mn
	ZMTS + HS	3.750 ± 0.076	10.194 ± 0.32	6.519 ± 0.29	2.087 ± 0.052	Cu > Zn > Pb > Mn
	ZMTS + (PC + HS)	34.407 ± 0.023	21.211 ± 0.11	27.344 ± 0.58	6.659 ± 0.22	Pb > Zn > Cu > Mn

ZMTS = zinc mine tailing soil, PC = phosphatic clay, HS = humus soil. Values of distribution coefficient for non-amended and amended soil are represented as arithmetic mean of triplicates ± S.D.

tion is mainly attributed to surface adsorption or complexation. Ca is the main cation in the phosphatic clay. Singh et al. [16] have noticed the release of calcium and sorption of lead in 1:1 ratio (equal displacement of Ca by Pb) during dissolution of phosphate rock and formation of the fluoropyromorphite. Co-precipitation of Zn (0.088 nm) and Cu (0.087 nm) with Ca (0.118) in the presence of phosphate rock would be less likely to occur compare to Pb (0.118) [45]. Ma et al. [46] speculated the precipitation of amorphous to poorly crystalline Zn phosphate. The sorption of Pb, Cu, Zn and Mn on the phosphatic clay and humus rich soil may be explained by means of Irwings-Williams order with Cu among the first row of the transition metals forming the more stable complex with ligands. According to Hard soft acid base (HSAB) theory Pb, Cu and Zn (Lewis base) form stable complexes with carboxylic, phenolic, hydroxyl functional groups (Lewis acid) present in the humus rich soil [45].

Behavior of the Mn in soil is generally assumed to mediate by redox reaction. Mn can exist in several oxidation states, Mn oxides can exist in several crystalline or pseudocrystalline states, the oxides can form co-precipitation with Fe oxides. Its sorption is more complicated since it forms insoluble oxides in response to Eh-pH conditions. Mn is strongly adsorbed by clay minerals. Adsorption has been found to increase with increasing pH [32]. Less sorption of Mn in present studies may be attributed to its conversion from higher oxidation states to lower oxidation states due to competition of other heavy metals at the surface of the soil. Also, the highest selectivity sequence of Mn on ZMTS (Table 3) in spite of its lower electronegativity value seems to be related to its adsorption in fixed oxidation state. This trend varies when phosphatic clay and humus soil is added to ZMTS. In general, sorption on Mn on soils can be facilitated by several mechanisms; first, the oxidation of Mn to higher valence oxides and/or precipitation of insoluble compounds in soils subjected to wetting and drying, second, adsorption into the crystal lattice of clay minerals, and adsorption on exchange sites. In calcareous soils, chemisorptions on to CaCO₃ and following precipitation of MnCO₃ may play an important role. Presence of chelating agents is not able to form stable Mn complexes in soils because Fe or Ca can substitute for Mn [47].

4. Conclusions

The sorption efficacy of phosphatic clay and humus rich soil was studied towards heavy metals from the zinc mine tailing. The leachability data showed the sorption efficacy of phosphatic clay and humus soil around 90%, at pH 3.0. The shape of percolation curve and order of selectivity sequence calculated on the basis of distribution coefficient showed high affinity of Pb on phosphatic clay in the presence of humus soil as compared to Cu, Zn and Mn. These results clearly indicate that phosphatic clay together with humus soil could be used as a cost effective immobilizing agents for better immobilization of heavy metals.

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