KINETICS OF DESORPTION OF HEAVY METALS FROM POLLUTED SOILS: INFLUENCE OF SOIL TYPE AND METAL SOURCE

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Abstract. Kinetics of desorption of heavy metal ions (Cd, Cu, Ni and Zn) from the surface (0–15 cm) samples of an acidic soil (Inceptisol) and a neutral soil (Mollisol) spiked with inorganic salts of these metals or through an acidic sludge were studied by the column method. The rate of desorption of soil applied heavy metals was initially rapid and gradually declined with time. In general, the release of heavy metals from soils polluted by inorganic or sludge sources conformed to a multi-site model of first order kinetics; however, the release of Cd and Ni applied through inorganic sources to the neutral soil could be adequately accounted for by single-site model. The double-site model could adequately explain the release of Cd from sludge amended acidic soil and the release of Zn applied though inorganic salt or sludge to the neutral soil. In acidic soil, the apparent desorption rate coefficients of heavy metals applied through inorganic sources were higher than those for the sludge source. In neutral soil, however, the apparent desorption rate coefficients of heavy metals added through sludge were higher than for inorganic sources. Among the heavy metals, the higher apparent desorption coefficient value and percent desorption of Cd indicated a higher potential of this metal for leaching and ground water contamination. The results also suggested that the acidic soil pH might reduce the ability of the soil to naturally sequester heavy metal cations and lead to their leaching.

Keywords: desorption kinetics, heavy metals, sewage sludge, sorption, soil pH

1. Introduction

In terrestrial ecosystems, sorption-desorption reactions at the surfaces of soil colloids control the concentration of heavy metal in soil solution and hence the bioavailability, leaching and toxicity of these metals (Backes *et al.*, 1995). Compared with the numerous published studies on sorption of heavy metals by soils and soil constituents, however, there are relatively few researches that have examined desorption of these metals simulating natural soil conditions (McLaren *et al.*, 1998; Krishnamurti *et al.*, 1999; Glover *et al.*, 2002). The adsorption and desorption capacities of soils for heavy metals are also likely to depend on soil pH, cation exchange capacity, nature of metal ion and metal source etc. Effect of the pollution source on trace metal desorption is very important to predict the potential bioavailability and toxicity hazards caused by these metals in natural ecosystems.

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Since there is limited information about the effect of pollution sources and soil reaction on desorption of trace metals, the present investigation was carried out to examine the kinetics of desorption of heavy metals (Cd, Cu, Ni and Zn) from soils of acidic and neutral pH polluted by inorganic salts of these metals or by sludge.

2. Materials and Methods

2.1. SOIL AND SLUDGE SAMPLES

Surface (0–15 cm) samples of an acidic and a neutral soil were collected from the Vivekananda laboratory, District-Almora (29°37′N 79°40′E) and the Crop Research Centre, Pantnagar (29°37′N 79°40′E), respectively. Sludge was collected from Karula Nala (District-Moradabad, Uttar Pradesh), receiving all the sewage effluents from different metal industries and the municipal area. Soil samples were air-dried and ground with a wooden roller and then passed through a 2 mm sieve. Some properties of the soils used in the study are presented in Table I.

Sludge was enriched in heavy metals by adding 50 mL stock solution containing 2000 mg Zn and Ni each, 1000 mg Cd and 4000 mg Cu l^{-1} to one kg sludge. The metal enriched sludge was thoroughly mixed and incubated at room temperature (29° to 32° C) for one month. The enriched sludge had a pH of 5.2, 48 g organic C, 257.6 mg Ni, 2225.8 mg Zn, 1517.4 mg Cu, 53.8 mg Cd kg^{-1} sludge. Around 10 g metal enriched sludge was mixed with 15 g air-dry soil to represent sludge-polluted soil. The final contents of heavy metals added to the soils through the organic sludge amounted to 21.52 mg Cd, 606.96 mg Cu, 103.04 mg Ni, and 890.32 mg Zn/kg soil. To represent inorganically polluted soils, dilute stock solutions of heavy

TABLE I

Selected properties of soil samples used in the study

General soil properties		Acidic soil	Neutral soil
Mechanical analysis	Sand (%)	49.56	41.56
	Silt (%)	18.00	30.90
	Clay (%)	32.44	27.54
	Texture	Sandy clay loam	Clay loam
Other soil properties	pH (1:2)	6.13	7.00
	O.C. %	0.94	1.20
	Cation exchange capacity (cmol kg^{-1})	11.04	15.75
Total content (mg kg^{-1})	Cd	1.62	2.60
	Cu	34.18	24.00
	Ni	41.06	36.31
	Zn	134.71	109.61

metals were added to 25 g air-dry soil and the final contents of heavy metals added to soil through inorganic metal salts amounted to 20 mg Cd, 80 mg Cu, 40 mg Ni, and 40 mg Zn/kg soil. After treatment, soils were thoroughly mixed and incubated at room temperature for 15 days at field capacity moisture regime. Treated soil samples were digested in HF-$HClO_4$ and analyzed for total content of heavy metals by atomic absorption spectrophotometry (Page *et al*., 1982). For the acidic soil, treatment with inorganic salts resulted in 18.25 mg Cd, 127.26 mg Cu, 123.00 mg Ni and 258.76 mg Zn/kg soil while sludge treatment gave 21.49 mg Cd, 621.77 mg Cu, 151.79 mg Ni and 973.50 mg Zn/kg soil. In the case of neutral soil, treatment with inorganic salts resulted in 19.18 mg Cd, 158.89 mg Cu, 128.51 mg Ni and 343.00 mg Zn/kg soil while sludge treatment gave 21.00 mg Cd, 635.50 mg Cu, 164.63 mg Ni and 1015.01 mg Zn/kg soil.

2.2. DESORPTION STUDY

Glass columns (30 × 2.5 cm) were packed with 25 g of treated soils in duplicate. Desorption of metals was initiated by continuous flow of 0.005**M** $CaCl_2$ at a flow rate of 0.15 mL/min. A constant head of 0.005**M** $CaCl_2$ solution was maintained in the column throughout the desorption period (up to 72 h). Eluted fractions were collected at 0.5, 1, 2, 4, 6, 8, 10, 12, 24, 48, 72 h. Heavy metals in each eluted fractions were determined by atomic absorption spectrophotometry.

The desorption data were fitted to the following first order equation:

$$c_t = \sum_{i=1}^{n} c_i \exp(-k_i t) \tag{1}$$

where, c_t is the concentration of metal remaining on the soil at time t, c_i is the initial concentration of metal on site i and k_i is the apparent desorption rate coefficient for metals bound by site i. Equation 1 was formulated with the assumption that all metal ions would desorb at $t = \infty$ i.e. $c_1 + c_2 \cdots + c_n = c_0$ (initial concentration of metal on soil at time t_0). In cases where a single site first order reaction was good enough to account for the observed data, c_i was taken as equal to c_0. Wherever, two sites first order reactions were noted, the fitting of experimentally observed values was done by optimizing values of c_1 (concentration of metal associated with the faster of the two first order reactions) and c_2 (concentration of metal associated with the slower of the two first order reactions). In case(s), where three-sites first order reactions were recorded, the fitting of experimentally observed values was done by optimizing values of c_1 (concentration of metal associated with the initial fastest of the three first order reactions), c_2 (concentration of metal associated with the relatively faster of the last two first order reactions) and c_3 (concentration of metal associated with the relatively slower of the last two first order reactions). Since the value of c_0 was fixed by the experimental data, the values of c_2 were considered as

$c_0 - c_1$ for two sites first order reactions and of c_3 as $c_0 - (c_1 + c_2)$ for three sites first order reactions.

The best fitting of equation was tested by coefficient of determination (R^2 at $p = 0.01$ and 0.05) and mean square deviation value (M.S.D.). The M.S.D. values were calculated according to Equation 2.

$$\text{M.S.D.} = \left[\frac{\frac{1}{(\text{Obs.Log}\, c_t)^2}(\text{Pred. Log}\, c_t - \text{Obs. Log}\, c_t)^2}{n-2} \right] \tag{2}$$

2.3. STATISTICAL ANALYSIS

Statistical analysis of the data was performed by the procedures outlined by Snedecor and Cochran (1967). The test of significance (F-test) was examined at probability levels of 1 and 5 per cent.

3. Results

3.1. DESORPTION OF HEAVY METALS FROM TREATED SOILS

In general, the desorption of heavy metals from soils spiked by inorganic salts or sludge was much faster for the initial few hours and then it became slower (Figure 1). Considering the absolute desorbed concentrations of different heavy metals, the ease of desorption was highest for Zn, followed by Cd and then Ni and least for Cu. In the acidic soil, the relative desorption of Zn and Cu was much higher under sludge treatment than under inorganic salt treatment possibly due to higher total content of these metals under sludge treatment. In spite of the lower total content of Cd and Ni under inorganic salt treatment as compared to the sludge treatment in the acidic soil, the relative desorption of Cd and Ni was, however, higher under the inorganic salt treatment indicating a higher mobility of Cd and Ni salts in acidic soil. In neutral soil, the relative desorption of all heavy metals selected for this study was higher under sludge than inorganic salts treatment due to higher total content of these metals under sludge treatment. However, for the neutral soil, the differences between inorganic salts and sludge sources for desorption of Cd and Ni in particular were narrower than for the acidic soil.

3.2. KINETICS OF HEAVY METALS DESORPTION

Initially, the graphs between log (c_t/c_o) and t were closely examined for the distribution pattern of observed values and linearity (graph not shown here). It was found that the desorption of Cd and Ni from the neutral soil polluted by inorganic salts followed a perfect linear relationship between log (c_t/c_o) and t thereby, indicating

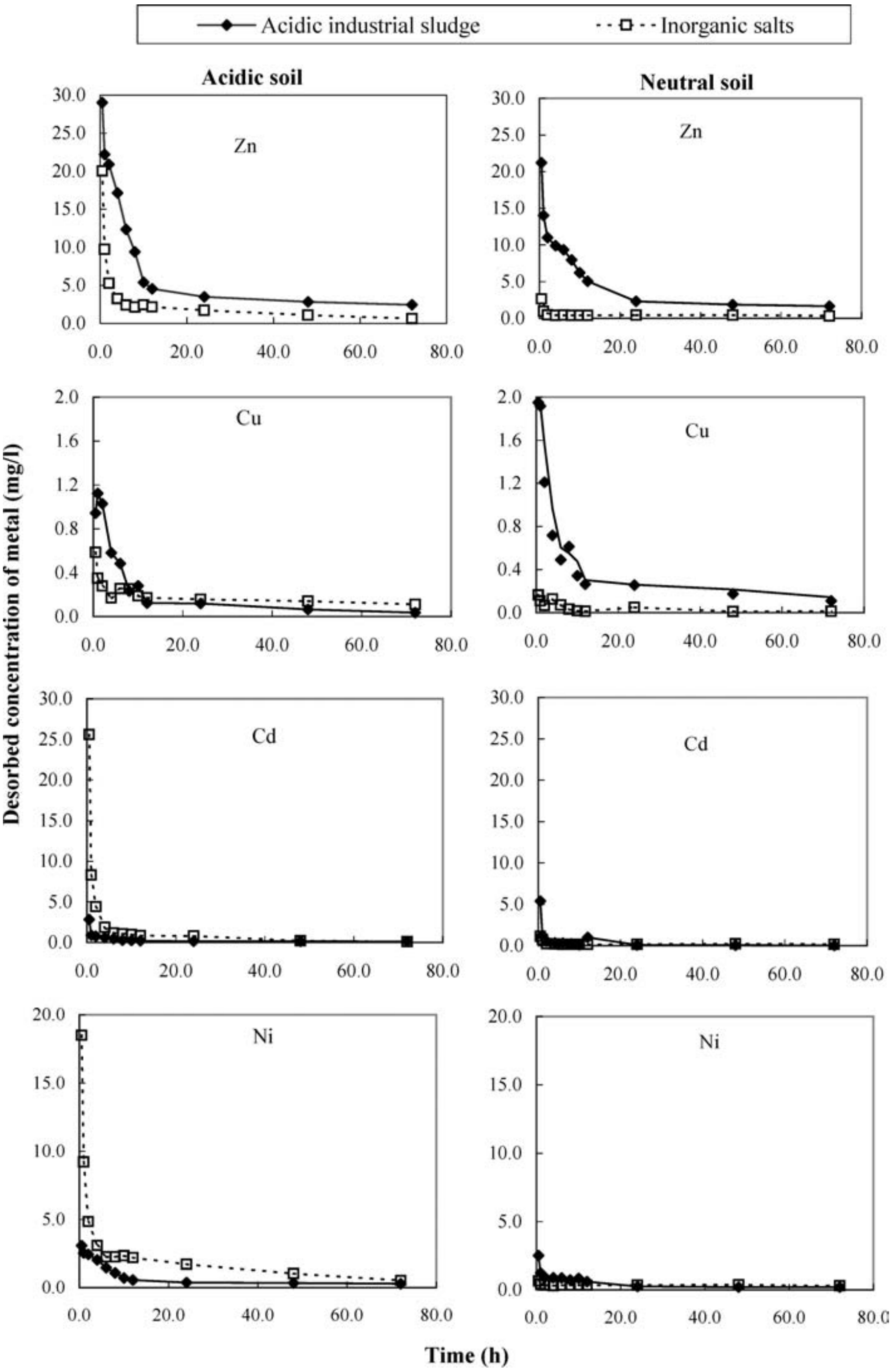

Figure 1. Desorption kinetics of heavy metals from soils spiked with inorganic salts or sludge. (Mean values of two replications)

the adequacy of single site first order model to explain the desorption behavior of these metals in the neutral soil. The graphs for desorption of Cd from sludge polluted acidic soil, of Zn from neutral soils polluted by either sludge or inorganic salts and of Ni from neutral soil polluted through inorganic salts could be resolved into only two distinct phases; a fast desorption and also a relatively slower desorption and the double site model was satisfactory to explain metal desorption. However, in all remaining cases the patterns of points indicated that desorption of heavy metals from soils receiving sludge and inorganic salts could be better resolved into three distinct phases; each one obeying first order kinetics.

Based on these observations, the experimental data were fitted into Equation 1 and values of apparent desorption coefficients and coefficients of determination (R^2) were computed. The predicted values of c_t at each time were computed using values of k_i and c_i. The calculated values of apparent desorption coefficients (k_i), coefficients of determination (R^2) and MSD calculated by Equation 2 are presented in Table II.

The values of coefficients of determination (R^2) were significant either at 1% or 5% level of significance except for a few cases where possibly lesser number of data points led to a statistically non-significant value of R^2. In general, apparent desorption rate coefficients of heavy metals in inorganic salts polluted acidic soil were higher than those of sludge polluted ones except in the case of Cu where the differences between sludge and inorganic salts for k_1 and k_2 were relatively narrower. On the other hand, apparent desorption rate coefficients of heavy metals in sludge polluted neutral soil were higher as compared to the values obtained for the inorganic salts polluted soil. This could be anticipated in view of the partly higher total content of heavy metals in the sludge polluted sample than inorganic salts polluted sample of neutral soil and also increased solubilization of organic matter and complexation reaction between solubilized organic ligands and heavy metals in neutral soil.

The relationships between experimentally observed and predicted values of metals sorbed by soils polluted by sludge or inorganic salts at different desorption periods are depicted in Figure 2. Low values of M.S.D. presented in Table II also indicated that the suggested number of desorption sites could successfully explain desorption of heavy metals from soils polluted by sludge or inorganic salts.

3.3. PERCENT DESORPTION OF HEAVY METALS

The data on percent desorption of heavy metals (percentage of total content of respective metal desorbed in treated soils) as per desorption patterns and also the % of total desorption accounted by different site(s) reactions in soils receiving sludge and inorganic salts are presented in Table III.

It is evident from the data that percent desorption of all heavy metals viz. Zn, Cu, Cd and Ni was higher in the acidic compared to the neutral soil. However, desorption of Cu from sludge treated neutral soil was higher than desorption observed in sludge

TABLE II

Desorption rate coefficients of heavy metals from soils polluted through inorganic salts and sludge (first order kinetics-multisite model)

		Acidic soil			Neutral soil		
Heavy metals	Source	Apparent desorption rate coefficients ($K_i \times 10^3$)	R^2 value	Mean square deviation (MSD × 10^3)	Apparent desorption rate coefficients ($K_i \times 10^3$)	R^2 value	Mean deviation square (MSD × 10^3)
Cd	Sludge	−150.66	0.979**	0.834	−2823.14	0.934	0.332
		−1.06	0.998**		−36.31	0.979*	
					−1.68	0.800	
	Inorg. salt	−345.75	0.999**	7.385	−1.77	0.997**	2.219
		−134.29	0.979				
		−15.95	0.998*				
Cu	Sludge	−253.52	0.994*	0.108	−266.35	0.999**	0.110
		−178.39	0.937		−166.01	0.998*	
		−0.01	0.972		−0.08	0.877*	
	Inorg. salt	−248.22	0.998*	11.504	−110.54	0.993*	11.457
		−137.81	0.991*		−172.92	0.999*	
		−0.16	0.995*		−0.01	0.998*	
Ni	Sludge	−189.43	0.996*	0.058	−181.70	0.999**	0.019
		−155.61	0.993*		−138.58	0.958	
		−0.30	0.998*		−0.20	0.999**	
	Inorg. salt	−265.99	0.998*	0.459	−0.43	0.999**	0.057
		−121.92	0.974				
		−1.29	0.972				
Zn	Sludge	−163.88	0.990**	0.036	−96.47	0.962**	0.019
		−169.62	0.999**		−0.30	0.997**	
		−0.47	0.999*				
	Inorg. salt	−567.22	0.999**	0.111	−76.17	0.954**	0.004
		−101.88	0.953*		−0.18	0.993**	
		−0.59	0.981				

treated acidic soil. This could be ascribed to more solubilization of organic ligands present in sludge in neutral soil and complexation of Cu by these ligands.

With regard to the extent of desorption of different heavy metals from the soil receiving inorganic salts or sludge, these metals could be arranged in the following order: Cd > Zn > Ni > Cu (Acidic and neutral soils treated with sludge) and Cd > Ni > Zn > Cu (Acidic and neutral soils treated with inorganic salts). Among heavy metals, the highest percent desorption of Cd from soil receiving sludge (22.31% and 18.45% in acidic and neutral soil, respectively) or inorganic

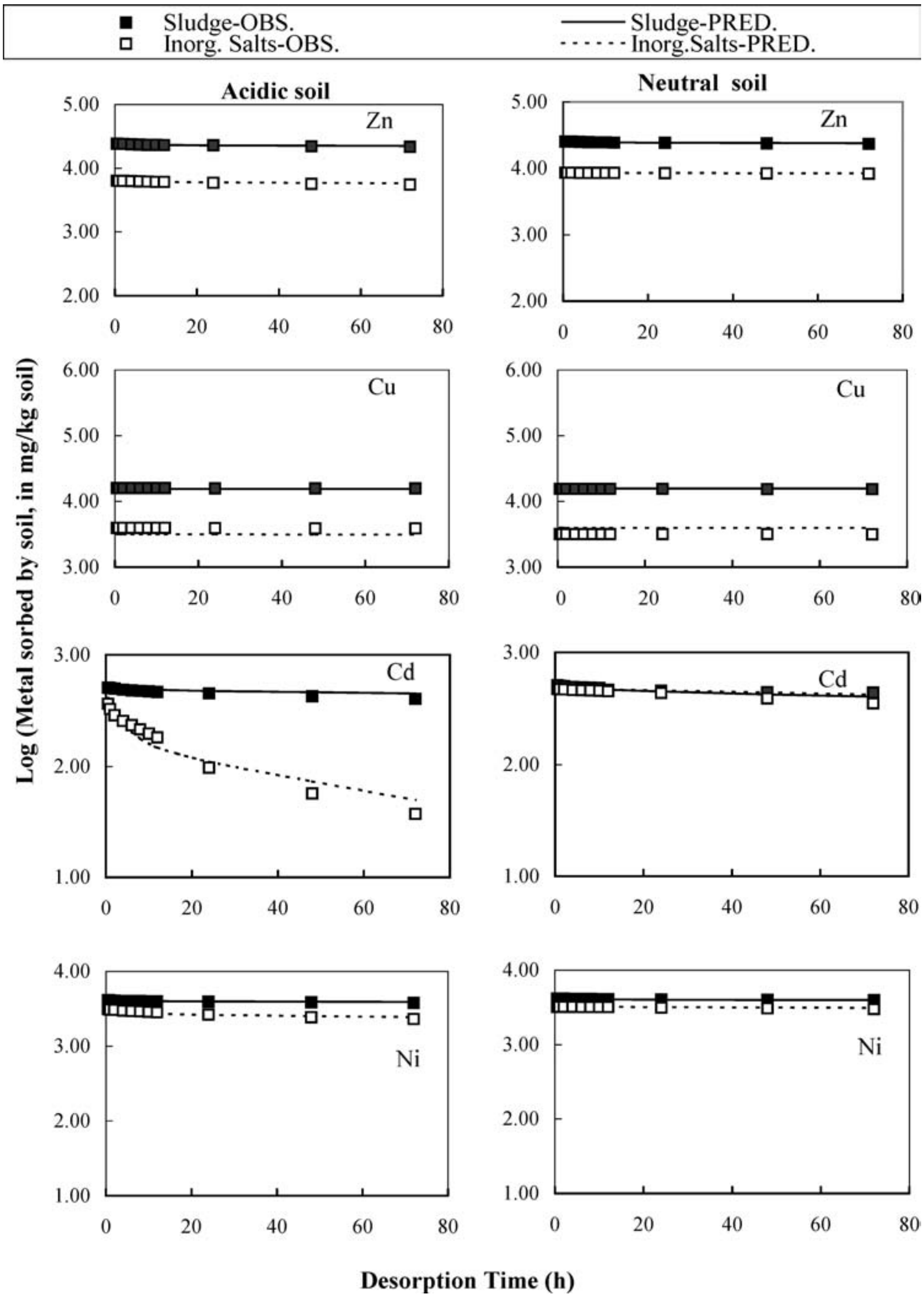

Figure 2. Metals sorbed on soil treated with inorganic salts or sludge at different desorption periods. Symbols show experimentally observed values and lines indicate fit to Equation 1.

TABLE III

Per cent (%) desorption and % of total desorption of heavy metals as per multi-site desorption model in soils polluted through inorganic salts and sludge

			Multi-site model			
			Acidic soil		Neutral soil	
Heavy metals	Source	R	%des. ± σ	%T	%des. ± σ	%T
Cd	Sl	1	10.35 ± 0.07	46.40	6.60 ± 0.05	35.77
		2	11.96 ± 0.08	53.60	6.75 ± 0.05	36.59
		3	–	–	5.10 ± 0.04	27.64
	I	1	49.41 ± 0.35	50.79	26.51 ± 0.16	100.0
		2	16.17 ± 0.11	16.61	–	–
		3	31.72 ± 0.22	32.60	–	–
Cu	Sl	1	0.19 ± 0.00	34.54	0.26 ± 0.00	25.69
		2	0.13 ± 0.00	23.97	0.19 ± 0.00	19.18
		3	0.22 ± 0.00	41.49	0.56 ± 0.00	55.23
	I	1	0.31 ± 0.00	10.22	0.10 ± 0.00	24.47
		2	0.49 ± 0.00	16.07	0.06 ± 0.00	14.03
		3	2.24 ± 0.02	73.71	0.26 ± 0.00	61.50
Ni	Sl	1	2.01 ± 0.01	25.49	1.00 ± 0.01	19.87
		2	1.64 ± 0.01	20.79	1.32 ± 0.01	26.05
		3	4.25 ± 0.03	53.72	2.73 ± 0.02	54.08
	I	1	7.28 ± 0.05	24.75	6.86 ± 0.05	100.0
		2	5.29 ± 0.04	17.99	–	–
		3	16.84 ± 0.12	57.26	–	–
Zn	Sl	1	3.90 ± 0.03	33.68	3.39 ± 0.02	43.77
		2	1.43 ± 0.01	12.36	4.35 ± 0.03	56.23
		3	6.24 ± 0.04	53.96	–	–
	I	1	4.37 ± 0.03	29.39	0.58 ± 0.00	18.48
		2	10.52 ± 0.07	70.61	2.55 ± 0.02	81.52

Sl = Sludge, I = Inorganic salt, R = Reaction, % des.= % desorption calculated as percentage of total content of heavy metal, ±σ = standard deviation, % T = Percent of total desorption accounted by two or more desorption sites.

salt (97.30% and 26.51% in acidic and neutral soil, respectively) indicated potential danger of Cd pollution in ground water and vegetation supported on polluted soils.

Percent desorption values estimated from multi-site model indicated that desorption of heavy metals was likely to occur through at the most three reactions except for a few exceptions. These exceptions included desorption of Cd and Ni from the inorganic salt polluted neutral soil, of Cd and Zn from sludge treated acidic soil and of Zn from sludge or inorganic salt polluted neutral soil. In general, desorption by the slowest reaction contributed at maximum often more than 50% of the total desorption.

4. Discussion

Initial faster desorption of heavy metals from soil indicated the release of these metals from the water-soluble fraction and also from the adsorption sites of lower bonding energy (exchangeable fraction). Slower desorption of metals indicated release of metals from sites of relatively higher bonding energy than the exchangeable form and other chemical pools in dynamic equilibrium with the exchangeable form. Krishnamurti *et al.* (1999) also noted similar involvement of sites of differing reactivity in Cd desorption from soils. Considering the absolute values of desorbed concentrations of different heavy metals, the ease of desorption was highest for Zn followed by Cd, Ni and Cu. The observed trend for ease of desorption coincided with the decreasing order of their bonding energies. Forbes *et al.* (1976) reported a similar decreasing order of intrinsic affinities of these metal ions to oxide surfaces. Lower desorption of these metals in neutral soil as compared to acidic soil could be related to changes in the type of surface complex and surface precipitation of these metals and higher net negative charge at relatively higher soil pH value (McBride, 1994).

Desorption data fitted well to first order kinetics. The release of Cd and Ni applied through an inorganic source to the neutral soil could be adequately accounted for by the single-site model indicating the presence of sites of uniform energy responsible for releasing these metals in the neutral soil. The release of Cd from sludge amended acid soil and the release of Zn applied though inorganic salt or organic sludge to the neutral soil could be adequately explained by the double-site model. The other desorptions were fitted well to a multi-site model indicating thereby the release of metals from heterogenous sites.

In general, the apparent desorption rate coefficients for the rapid desorption phase were higher than those for the slower desorption phases. Similar results were obtained for Zn and Cd desorption by Kuo and Mikkelsen (1980) and Backes *et al.* (1995), respectively. Lehmann and Harter (1984) reported that an initial rapid release of Cu; followed by a slow reaction, indicated that Cu was held by two types of sites: the rapidly released Cu being loosely held on the soil surface and the slowly released Cu being tightly bound.

Among heavy metals, the higher percent desorption of Cd from soil receiving organic or inorganic sources indicated potential danger of Cd pollution on heavy metal polluted soils.

5. Conclusion

The desorption of heavy metals from soils polluted by inorganic or organic sources conformed to the first order kinetics. The desorption of heavy metals added in the inorganic form was higher in the acidic soil while through sludge source the release was higher in the neutral soil. Among heavy metals, the highest apparent desorption rate coefficient and percent desorption of Cd indicated a higher potential of this metal to pollute ground water and vegetation at disposal sites of Cd containing waste. The percent desorption of Cd was also higher for inorganic salts especially, in acidic soil.

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