Research Article

Exchange Characteristics of Lead, Zinc, and Cadmium in Selected Tropical Soils

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Conducting binary-exchange experiments is a common way to identify cationic preferences of exchangeable phases in soil. Cation exchange reactions and thermodynamic studies of Pb^{2+}/Ca^{2+}, Cd^{2+}/Ca^{2+}, and Zn^{2+}/Ca^{2+} were carried out on three surface (0–30 cm) soil samples from Adamawa and Niger States in Nigeria using the batch method. The physicochemical properties studies of the soils showed that the soils have neutral pH values, low organic matter contents, low exchangeable bases, and low effective cation exchange capacity (mean: 3.27 cmolc kg^{-1}) but relatively high base saturations ($\gg$50%) with an average of 75.9%. The amount of cations sorbed in all cases did not exceed the soils cation exchange capacity (CEC) values, except for Pb sorption in the entisol-AD2 and alfisol-AD3, where the CEC were exceeded at high Pb loading. Calculated selectivity coefficients were greater than unity across a wide range of exchanger phase composition, indicating a preference for these cations over Ca^{2+}. The K_{eq} values obtained in this work were all positive, indicating that the exchange reactions were favoured and equally feasible. These values indicated that the Ca/soil systems were readily converted to the cation/soil system. The thermodynamic parameters calculated for the exchange of these cations were generally low, but values suggest spontaneous reactions.

1. Introduction

Baseline concentration of heavy metals in soils depends on the local geology. This has been supplemented to various degrees by anthropogenic inputs from industrial processes and operations that generate wastes containing considerable amounts of these metals. Heavy metals are nonbiodegradable and hence environmentally persistent and may accumulate in biota and the soils where they can affect soil properties. They interact with soils in various ways but sorption from aqueous solution onto solid particles is an important process that influences their accumulation and transport in the environment [1]. Thus, heavy metals pollution in soils has become a significant topic of concern.

Nowhere has the situation become more serious than in developing countries due to the recent establishment of industries producing wastes and effluents containing heavy metals. This has led to increase in the heavy metal burden of the developing countries where waste management practices are poor and the final metal sink is the soil. Metals may interact with soils in many ways: they may be sorbed by the soil depending on the soil pH, organic matter content, cation exchange capacity, and so forth; the oxidation state of some metals may be changed, thus affecting their mobility, bioavailability, and toxicity [1]. Our major concern is however the displacement of the major exchangeable cations, Ca, Na and K, by toxic heavy metals, thus increasing their chances of absorption by plants and consequently man via the food chain [2].

Furthermore, due to the selective retention and competitive adsorption by the soil, there is the tendency of increasing the concentration of these elements in the soil

beyond tolerable limits. Thus, the movement of these metals into the food chain may be enhanced with possible deleterious effects on human health and ecological balance [3, 4]. Therefore, understanding and minimizing soil pollution and degradation is of fundamental importance and deserves the highest priority in order to protect our food supplies from toxic substances which can accumulate in the soil. Understanding how these cations compete for exchange sites in soils, at varying concentrations and saturations on the exchanger relative to a typical cation (e.g., Ca), would provide useful information about their selectivities and, thus, mobility in soils. Equilibrium thermodynamic studies were used to explain the behaviour of cations in soils, and data obtained from the studies can then be applied not only to predict which of the soil processes are likely to occur, but also to estimate the solution metal composition at equilibrium since the aqueous fractions are of primary importance when considering the migration potentials of metals associated with soils.

Cd and Pb belong to the most potentially toxic heavy metals. Classified as soluble and strongly hydrating cations, both metals are particularly toxic to plants and higher animals, producing kidney and blood diseases among other health disorders [5]. The ever increasing use of Zn in many products is assuming a frightening dimension as scientists are showing proofs of harmful effects on living things of high concentration of Zn [1]. The presence of these cations in soils can affect the plant intake of major cations (Ca, Mg, and Na) which are adsorbed primarily by cation exchange, a readily reversible sorption mechanism caused by electrostatic attraction of cations to negatively charged surfaces [6]. Thus, we have done adsorption of these metals from binary metal solutions using three soils representative of the entisol and alfisol soil groups [7] so as to understand the mobility of these metals in soil in the presence of other metals.

2. Materials and Methods

2.1. Soil Sampling, Pretreatment, and Characterization. Three surface (0–30 cm) soil samples were obtained from Adamawa and Niger States of Nigeria (Table 1). The samples were air dried, crushed gently, and sieved through a 230-mesh size sieve, and fine particles were retained for the study. The soils' pH was determined in deionized water and 1.0 M KCl (in ratio 1 : 1). Particle size determination was by the hydrometer method [8], organic carbon was by the Walkley-Black wet digestion method [9], cation exchange capacity (CEC) was by the 1.0 M ammonium acetate (NH_4OAC) method at pH 7.0 from the extractable bases: Na and K [10], and exchangeable Ca and Mg were determined from 1.0 M sodium acetate extracts at pH 7.0 [11]. Total nitrogen, base saturation, exchangeable acidity, exchangeable micronutrients, and trace heavy metals were also determined [12]. Elements in the extracts were determined using the Buck Scientific 205 Atomic Absorption Spectrometer (AAS).

2.2. Preparation of Ca Homoionic Saturated Soils. About 100 g each of the samples was first suspended in 1.0 M NH_4OAc for 2 hours to obtain the NH_4^+-saturated soils.

TABLE 1: Sample description.

| Location/sample collection point	Sample code	Soil class	Coordinate
Along River Benue Bank	AD2	Entisol	$9°20'N; 12°30'E$
Girei Local Government Area	AD3	Alfisol	$9°20'N; 12°30'E$
New Bussa	NB	Alfisol	$9°53'N; 4°31'E$

These were filtered, dried at 105°C, and then resuspended in 1.0 M $CaCl_2$ solution, mechanically agitated gently for 45 minutes, and left to stand overnight with periodic mechanical agitation. After 16 hours, the suspensions were then filtered under suction and washed with fresh 100 mL of the saturating solution. The Ca-saturated soils were then washed with 400 mL of deionized water in 100 mL potions and then equilibrated for a further 72 hours. After this, the soils were each filtered and washed first with 100 mL $CaCl_2$ solution, then 200 mL deionized water, and with about 350 mL ethanol, all in 100 mL portions until free from chloride [13]. The soils were then transferred into Petri dishes, dried in an oven at 105°C for about 5 hours, homogenized, and then stored for Ca/Pb, Ca/Cd, and Ca/Zn exchange studies as appropriate.

2.3. Preparation of Equilibrating Solutions. Equilibrating solutions were prepared by using six predetermined mole fractions of the metal (M^{2+}). Mole fractions ranged from 0.0 to 1.0, while maintaining a constant ionic strength of 0.003. The concentrations were prepared by transferring accurately 0/30, 20/24, 40/18, 60/12, 80/6, and 100/0 mL volumes of 0.01 M $M^{2+}Cl_2$/0.01 M $CaCl_2$, respectively, into six 1-litre standard flasks and diluted to mark with deionized H_2O [14]. $NaNO_3$ was used as the indifferent electrolyte.

2.4. Batch Equilibration Method. Replicate batch equilibrations were achieved by adding 50 mL of equilibrating solution to 1.0 g of Ca-saturated soil in 120 mL polypropylene tubes and intermittently shaking the capped bottles mechanically at room temperature (26 ± 2°C) for 24 hours. The suspensions were then filtered and the supernatant retained for the estimation of Ca, Pb, Zn, and Cd using the Buck Scientific 205 AAS with air-acetylene flame on absorbance mode. The same procedure was repeated at 60°C in an incubator maintained at 60 ± 2°C for 24 hours. All experiments were done, in duplicate and in all cases, the experimental errors were <1%.

2.5. Data Treatment

2.5.1. Exchange Calculations. Equation (1) will be used for representative illustration for Ca/Pb exchange reaction

$$Ca_{(s)}^{2+} + Pb_{(aq)}^{2+} \rightleftharpoons Ca_{(aq)}^{2+} + Pb_{(s)}^{2+} \qquad (1)$$
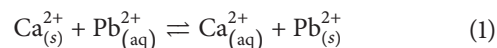
The concentration of the ions in the adsorbed phases, in mmol kg^{-1}, was calculated from the difference between the total ion before and after equilibration. Equilibrium data obtained for the soils at 30°C and 60°C were used to calculate the

relative amounts of Pb^{2+} and Ca^{2+} ions in solution (as mole fraction of $Pb^{2+} = XPb^{2+}$) and those of the soil phase (as equivalent fraction of $Pb^{2+} = X'Pb^{2+}$) at equilibrium. Hence, the equivalent ratios of Ca^{2+} and Pb^{2+} in both phases were calculated from the following relationships:

$$X'_{Ca^{2+}} = \frac{[Ca^{2+}]'}{([Ca^{2+}]' + [Pb^{2+}]')}, \quad (2)$$

$$X'_{Pb^{2+}} = \frac{[Pb^{2+}]'}{([Pb^{2+}]' + [Ca^{2+}]')}, \quad (3)$$

$$X_{Ca^{2+}} = \frac{[Ca^{2+}]}{([Ca^{2+}] + [Pb^{2+}])}, \quad (4)$$

$$X_{Pb^{2+}} = \frac{[Pb^{2+}]}{([Pb^{2+}] + [Ca^{2+}])}, \quad (5)$$

where $[Ca^{2+}]'$ and $[Pb^{2+}]'$ are equivalent concentrations of Ca and Pb in the soil phase while $([Ca^{2+}]' + [Pb^{2+}]')$ is the total equivalent concentration of the cations, Ca and Pb, in the soil phase. $[Ca^{2+}]$, $[Pb^{2+}]$, and $([Ca^{2+}] + [Pb^{2+}])$ are the corresponding values in solution and $X_{Pb^{2+}}$ and $X_{Ca^{2+}}$ are equivalent fractions of the exchanging Pb^{2+} and Ca^{2+} in the soil phase.

2.5.2. Exchange Selectivity Coefficients and Other Thermodynamic Constants. The exchange selectivity coefficients (K_c) were calculated according to Gaines and Thomas [15] (equation (9)), where M^{2+} and Ca-soil refer to bivalent and the soil phase metals, respectively,

$$M^{2+}_{aq} + Ca - Soil \rightleftharpoons M - Soil + Ca^{2+}_{aq} \quad (6)$$
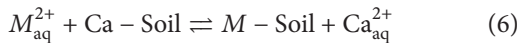
The selectivity coefficient K_c has been defined [16] as

$$K_c = \frac{M_{Ca^{2+}} \cdot X_{Pb^{2+}} \cdot \gamma_{Ca^{2+}}}{M_{Pb^{2+}} \cdot X_{Ca^{2+}} \cdot \gamma_{Pb^{2+}}}, \quad (7)$$

where $M_{Ca^{2+}}$ and $M_{Pb^{2+}}$ are the molarity of cations (Ca^{2+} and Pb^{2+}) in equilibrium. $X_{Pb^{2+}}$ and $X_{Ca^{2+}}$ are the same as above. The activity coefficients, γ_x, are calculated from the modified Debye-Huckel law [17] in the following:

$$\log \gamma_x = AZ_x^2 \left\{ \frac{\sqrt{I}}{(1 + \sqrt{I})} - 0.3I \right\}, \quad (8)$$

where Z_x is the ion valence, A is a temperature dependent constant, which is obtained from the literature as 0.5141 and 0.5471 per unit volume of solution at 30°C and 60°C, respectively, γ_x could be either $\gamma_{Ca^{2+}}$ or $\gamma_{Pb^{2+}}$, and I is the ionic strength of the solution. In this work, I is fixed at 0.003. Usually, γ_x for metals of the same valence is equal and thus has been calculated for the divalent cations used as 1.2733 at 30°C and 1.2932 at 60°C.

Equilibrium constants in this study were obtained by integrating the cation selectivity coefficients over the whole range of exchange isotherm and so may be interpreted in terms of the overall preference of an exchanger for one out of a pair of exchangeable ions:

$$\ln K_{eq} = -(Z_{1-}Z_2) + \int_0^1 \ln K_c d\overline{X}_M. \quad (9)$$

Since both exchanging cations are bivalent, $(Z_{1-}Z_2)$ gives zero and thus (9) becomes

$$\ln K_{eq} = \int_0^1 \ln K_c d\overline{X}_M. \quad (10)$$

X_M is the equivalent fraction of cation on the exchanger; K_{eq} is the equilibrium constant.

To obtain $\ln K_{eq}$, the integral term of (10) above is evaluated graphically:

$$\ln K_{eq} = x \ln K_c + C,$$
$$\ln K_c = \left(\frac{1}{x}\right) \ln K_{eq} - \left(\frac{C}{x}\right), \quad (11)$$

where $\ln K_{eq}$ is the slope and C/x is the intercept.

Once the $\ln K_{eq}$ was obtained, the Gibbs free energy ($\Delta G°$), $\Delta H°$, and ΔS values for the exchanger reaction (at a specified temperature, T) can be computed from the following:

$$\Delta G° = -RT \ln K_{eq},$$
$$\Delta G° = \Delta H° - T\Delta S°,$$
$$\ln \left(\frac{K_2}{K_1}\right) = \left(\frac{\Delta H°}{R}\right) \{T_2^{-1} - T_1^{-1}\}, \quad (12)$$

where ΔH is the enthalpy change, measured in kilojoules per mole, R is the gas constant, T_1 and T_2 are the lower and higher absolute temperatures, and K_1 and K_1 are the equilibrium constants at T_1 and T_2, respectively.

3. Results and Discussion

3.1. Soil Properties. The samples and their physicochemical characteristics are shown in Tables 1 and 2. The soils have been classified as entisol (AD2) and alfisols (AD3 and NB-); however, particle size distributions showed that textural classes for AD2, AD3, and NB are loam, loamy sand, and sandy loam, respectively [7]. The pH of the soils measured in both 1:1 deionized water and 1.0 M KCl showed that the soils can be classified as neutral. A value of ≈1.0 for ΔpH was observed in the soils ($pH_{KCl}-pH_{H_2O}$) indicating that a slight negative charge is present in each soil as H^+ and OH– interact with the soils' surface. These pH values were within the range found for mineral soils in typical Tropical Nigeria soils [13, 18].

The percentage soil organic carbon contents for AD2 (3.81) and NB (2.82) are high while those of AD3 (1.15) are

TABLE 2: Physicochemical properties of the soil samples.

Sample	pH		Org. C	T. N	Exchangeable bases (cmolc kg^{-1})				CEC	Base sat.	Particle size analysis (%)		
	KCl	H$_2$O	%	%	Ca	Mg	Na	K	Meq/100 g	%	Sand	Silt	Clay
AD2	6.6	7.6	3.8	0.5	1.5	0.8	0.1	0.2	3.6	71.8	51.2	31.4	17.4
AD3	5.7	6.7	1.2	0.3	1.6	0.7	0.1	0.2	3.6	72.2	81.2	11.4	7.4
NB	6.5	7.4	2.8	0.4	1.4	0.7	0.1	0.2	2.9	79.5	53.2	27.4	19.2

Org. C: organic carbon; T. N.: total nitrogen; CEC: cation exchange capacity; Base sat.: base saturation.

described as medium [19] with sequence: AD3 < NB < AD2. Olu-Owolabi et al. [18] and Igwe et al. [20] have reported organic carbon contents of similar range for soils in the West African savannah. The relatively high organic matter content value of AD2 and NB may not be unrelated to the rich deposit of organic materials brought inland by tidal action from the rivers Benue and Niger, respectively.

Sum of exchangeable bases for samples AD2 (2.6 cmolc kg^{-1}), AD3 (2.6 cmolc kg^{-1}), and NB (2.3 cmolc kg^{-1}) (Table 2) are described as low [19]. The sequence of total abundance is NB < AD2 < AD3. All samples showed exchangeable bases abundance in the order Ca > Mg > K > Na. The predominance of Ca may be a common feature of Nigerian soils [13, 18], and this may be linked to the fact that soils in the subhumid regions are majorly dominated by low activity clay minerals and low organic matter content. The soils all have CEC values that can be described as low [19]. These values agree with results obtained from other studies on Nigerian soils [13, 18, 19]. The CEC sequence for these soils is NB < AD2 < AD3.

3.2. Selectivity Coefficient (K_c).
The selectivity coefficient, K_c, quantifies the preference of the adsorbent for a given cation from a pair, exchanging at its surface at a given solution ratio [21]. Although it is independent of the total ionic strength of the solution bathing the exchanger [22], it is common experience that this quantity varies with ion composition of the exchanger phase. Generally, but not always, it decreases with increasing saturation of the preference cation on the exchanger surface [23].

Values of the experimentally determined selectivity coefficients for the Ca-cation exchange reactions on all soil samples are shown in Table 3. In the Ca^{2+} → M^{2+} exchange equilibrium, the K_c varied continuously with cationic composition of the soil surfaces. Overall, the selectivity coefficients (K_c) were relatively irregular with most values greater than 1. The values of K_c were maximum for intermediate values of $X'M$. In the NB soil, the amount of cations adsorbed did not exceed the soil CEC value; but, for Pb sorption in AD2 and AD3 soils, it was exceeded at very high Pb loading, indicating other Pb sorption mechanisms in addition to cation exchange (Table 3). Selectivity coefficients of the soils varied continuously with their surface cationic composition; thus, the higher the CEC, the higher the cation adsorption. Similar results have been reported by Robbins and Carter [24], Olu-Owolabi et al. [18] for soils in Western Nigeria, Sha'ato [13] for soils from the central Nigeria State of Benue, Godfrin et al. [25] for Ca^{2+} → Zn^{2+} exchange system, Gast

[23], and Angove et al. [26]. Depending on the soil, metal ion type, and concentration, temperature had varying effects on the exchange. Increased temperature favoured Kc for Pb adsorption in samples AD2 and NB; Zn in AD2, NB, and AD3; and Cd in AD3. However, increased temperature led to reducing Kc for Cd adsorption in AD2 and NB and Pb in AD3. The selectivity coefficient values of this study have shown that all three soils have a higher preference for the risk element than for Ca^{2+} in the order Cd^{2+} > Zn^{2+} > Pb^{2+}. In general, soil sample AD3 had the higher K_c values than samples AD2 and NB.

3.3. Equilibrium Constant (K_{eq}).
The K_{eq} values obtained in this work were all positive, indicating that the exchange reactions were favoured and equally feasible (Table 4). These values indicated that the Ca-soil systems were readily converted to the cation-soil system. The small values of K_{eq} for the Ca^{2+} → Pb^{2+} exchange systems in AD2 and NB indicated a reluctance of the Ca-soil complex to form the Pb-soil complex. This argument is also supported by the positive ΔG values for the same soils. Increased temperature had no effect on the Ca-Pb system for NB but led to a slight decrease for Cd adsorption in all soils and Pb adsorption in AD3. Slight increases were noticed in Zn adsorption in AD2, AD3, and NB and Pb in AD2. These slight decreases in K_{eq} especially for AD3 indicated ease of exchange for the cations.

3.4. Thermodynamic Equilibrium Parameters ($\Delta H°$, $\Delta G°$, and $\Delta S°$).
The values of the thermodynamic parameters are shown in Table 4. The ΔH values were low and in the range of 0.02–11.64 kJ mol^{-1} with a mean value of 0.65 kJ mol^{-1}. These small values of ΔH imply weak electrovalent bond interactions between soil and metal ions in the exchange process. Similar results have been reported by Sidhu et al. [27] and Sha'ato [13] for central Nigeria soils. These values were not compatible with the formation of strong chemical bonds between exchange sites in soil and metal ions, and the exchange process is likely to be on account of the easy breaking of these weak ionic bond interactions between Ca and soil exchange sites. These calculated enthalpy values are described as "apparent" because they were comprised of contributions from the energetic effects associated with intrinsic adsorption step and dehydration effects of the metal ions inside the aqueous solution, in addition to any plausible contribution from the physical/chemical changes that the sorption sites might undergo as a result of sorption.

TABLE 3: Selectivity coefficient, K_c, as a function of soil phase composition in $Ca^{2+} \rightarrow M^{2+}$ exchange at 30°C and 60°C in the different soils studied.

(a) Selectivity coefficient, K_c, for soil AD2

			AD2		
X'_{Cd}	K_c	X'_{Zn}	K_c	X'_{Pb}	K_c
			30°C		
0.00	0.00	0.00	0.00	0.00	0.00
0.30	33.05	0.43	5.54	0.46	0.67
0.43	50.89	0.61	14.49	0.69	1.05
0.71	19.62	0.77	10.08	0.83	1.24
0.86	10.30	0.91	4.14	0.93	1.35
1.00	0.00	1.00	0.00	1.00	0.00
			60°C		
0.00	0.00	0.00	0.00	0.00	0.00
0.32	23.06	0.42	5.72	0.46	0.65
0.42	44.26	0.57	17.88	0.68	2.03
0.73	12.84	0.76	9.60	0.83	1.67
0.87	7.20	0.91	3.77	0.92	2.21
1.00	0.00	1.00	0.00	1.00	0.00

(b) Selectivity coefficient, K_c, for soil AD3

			AD3		
X'_{Cd}	K_c	X'_{Zn}	K_c	X'_{Pb}	K_c
			30°C		
0.00	0.00	0.00	0.00	0.00	0.00
0.18	127.48	0.40	13.37	0.43	7.57
0.24	196.05	0.62	15.83	0.61	19.80
0.31	219.09	0.76	14.44	0.77	13.70
0.73	41.83	0.88	10.82	0.89	10.75
1.00	0.00	1.00	0.00	1.00	0.00
			60°C		
0.00	0.00	0.00	0.00	0.00	0.00
0.14	356.00	0.38	24.53	0.45	2.56
0.31	241.90	0.58	33.68	0.64	9.30
0.55	112.83	0.73	28.50	0.75	17.58
0.79	44.30	0.88	13.12	0.90	7.22
1.00	0.00	1.00	0.00	1.00	0.00

(c) Selectivity coefficient, K_c, for soil NB

			NB		
X'_{Cd}	K_c	X'_{Zn}	K_c	X'_{Pb}	K_c
			30°C		
0.00	0.00	0.00	0.00	0.00	0.00
0.34	24.06	0.42	6.03	0.46	0.18
0.48	39.50	0.65	7.23	0.69	0.53
0.68	24.71	0.79	7.65	0.83	1.03
0.88	8.50	0.92	2.64	0.93	1.00
1.00	0.00	1.00	0.00	1.00	0.00

(c) Continued.

			NB		
X'_{Cd}	K_c	X'_{Zn}	K_c	X'_{Pb}	K_c
			60°C		
0.00	0.00	0.00	0.00	0.00	0.00
0.36	17.64	0.41	8.44	0.46	0.13
0.51	28.85	0.61	12.84	0.69	1.78
0.72	16.82	0.75	11.84	0.83	1.39
0.88	7.22	0.91	3.68	0.93	1.23
1.00	0.00	1.00	0.00	1.00	0.00

The Gibb's free energy ($\Delta G°$) values were all negative, except for Pb exchange in AD2 and NB suggesting spontaneous reactions (Table 4). Hence, the "soil-heavy cation" complex formation was favoured. The $Ca^{2+} \rightarrow Pb^{2+}$ exchange complexes in AD2 and NB had positive $\Delta G°$ values; this may be due to the uncertainties in the estimation of thermodynamic parameters using linear plots of thermodynamic models which may introduce some errors that could shift values from the border of one extreme to another [28]. When this occurs, adsorption reactions that have small but negative ΔG could shift to small but positive ΔG values. This may be the case with the positive ΔG values obtained in this study, though A. S. Özcan and A. Özcan, [29] have shown that positive values for ΔG are quite common with ion-exchange mechanism of adsorption of cations. Overall, the sorption data showed that, at equilibrium, the tendency for these soils was towards spontaneous adsorption of the cations in preference to Ca^{2+}. Similar results have been reported by Alvarez-Ayuso and Garcia-Sanchez [30].

The $\Delta S°$ values were positive, except for Cd exchange in AD3 and NB, and Pb exchange in AD3, suggesting increased disorder at equilibrium. The positive entropy suggests increased disorder at equilibrium while the negative indicated otherwise. The increased entropy at equilibrium may be due to increase in the dehydration steps of the adsorbate ions, which are known to possess relatively high energies of solvation and thus are stabilized by water sheaths in the absence of the adsorbent. The reverse was the case for Cd exchange in AD3 and NB and for Pb exchange in AD3. Although positive entropy is theoretically associated with spontaneity, this does not suggest that exchanges with negative entropy were not spontaneous since enthalpy and entropy work to complement one another. These two factors are the major forces leading to the observed spontaneity of the exchange.

4. Conclusion

The soils studied in this work can be classified as "strong" acid exchangers because cation exchange was the major sorption mechanism observed. The amount of cations sorbed in most cases did not exceed the CEC values, except for Pb sorption in AD2 (entisol) and AD3 (alfisol) where it was slightly exceeded at very high Pb loading, indicating a specific Pb sorption mechanism in addition to cation exchange. Soil

TABLE 4: Thermodynamic data for adsorption on samples AD2, AD3, and NB.

	30°C K_{eq}	60°C K_{eq}	$\Delta G°$ (kJ mol^{-1}) at 30°C	$\Delta G°$ (kJ mol^{-1}) at 60°C	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (JK^{-1} mol^{-1})
AD2 Pb^{2+}	0.85	0.90	0.4176	0.2780	1.8288	4.66
AD2 Cd^{2+}	3.47	3.39	−3.1328	−3.3793	−0.6431	8.22
AD2 Zn^{2+}	2.72	2.84	−2.5181	−2.8893	1.2303	12.37
AD3 Pb^{2+}	3.10	2.05	−2.8524	−1.9828	−11.6352	−28.99
AD3 Cd^{2+}	2.77	2.21	−2.5678	−2.1924	−6.3587	−12.51
AD3 Zn^{2+}	3.38	4.33	−3.0678	−4.0590	6.9431	33.04
NB Pb^{2+}	0.46	0.46	1.9649	2.15730	0.0224	−6.41
NB Cd^{2+}	3.78	3.54	−3.3474	−3.4979	−1.8288	5.01
NB Zn^{2+}	2.52	2.97	−2.3259	−3.0133	4.6166	22.91

composition played a larger role than metal type in the patterns of selectivity for the cations studied. ΔG values indicated weak electrovalent bond interactions between the soils and metal ions and reactions were spontaneous and feasible. The soils preferentially adsorbed Pb, Zn, and Cd over Ca. AD2 and NB had higher adsorption capacity for these metals because of their higher organic matter and clay contents. These heavy metals in AD3 (Girei) will pose more challenge to biota as well as leach into ground water aquifer due to the reduced adsorptions and high concentrations in soil water solutions. Thus, for a sustainable soil use and development of suitable strategies for proper management of heavy metal soils, soil properties and nature of pollutant must be taken into consideration and thus the impact on environment can be minimized.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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