

Sorption and Desorption Phenomena of Urban Biowaste-Based Heavy Metals by a Ferralsol

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Abstract

Background: The objective of this study was to examine the adsorption-desorption phenomena of heavy metals in an agricultural Ferralsol treated with sewage solid waste at rates usually applied for soil fertility management. Methods: The study was carried out under laboratory conditions, using a Ferralsol sourced from Makerere University Agricultural Research Institute, Kabanyolo (MUARIK). Soil and sewage solid waste were analysed for pH, organic matter, cation exchange capacity and heavy metals (copper, zinc, chromium and lead). Soil was treated with sewage solid waste at input rates of 0, 50, 100, and 150 g per pot (equivalent to 0, 2.5, 5.0 and 7.5 metric tones ha^{-1} respectively); and supplemented with phosphorus. The phosphorus was applied at rates of 0, 0.795, 1.591 and 2.385 g per pot (equivalent to 0, 25, 50 and 75 kg·ha⁻¹, respectively). Batch adsorption was used to study the sorption-desorption of heavy metals on the treated soil and the Langmuir and Freundlich models were used to analyse the data. Results: Adsorption and desorption isotherms fitted better to Freundlich equation than Langmuir model. Chromium was the most sorbed and retained metal; while lead was the least retained overall. The desorption process was virtually irreversible, considering the low amounts of the metals desorbed. Chromium fitted relatively better to both models than the copper, zinc and lead. All the four metals were less desorbed at high metal concentrations. Conclusion: The four metals would not be available at high metal concentrations especially when the application rate used is \geq 5.0 tones ha⁻¹ of the sewage solid waste. Thus, the metals would not be available for plant uptake and the chance to contaminate groundwater is very limited especially for chromium.

Keywords

Heavy Metals, Sewage Solid Waste, Ferralsol, Sorption-Desorption

1. Introduction

Heavy metals and their compounds are a threat to environmental health, yet plants, aquatic life and humans continue to be exposed to the substances through industrial and unscreened agricultural inputs [1]. There is the crave for locally available soil amendments, for example biosolid wastes, to boost agricultural production, paralleled by efforts to free urban environments of obnoxious wastes such as sewage solid waste [2] [3]. Unfortunately, the materials are variously contaminated with heavy metals, mainly originating from industry wastewater (effluents), corrosion within the sewage system and rainwater runoff, which enter into the combined drainage system [4]. Thus, continued utilization of the materials without commensurate efforts to screen them for suitability for the purpose, or devision of effective mechanisms for their demobilization in the soil, is indeed a sure path to environmental and human health disaster [5] [6] [7].

The most frequent heavy metal contaminants in biosolids in sub-Saharan Africa include zinc (Zn), copper (Cu), lead (Pb) and chromium (Cr) [8] [9]. These have been reported to be prevalent in concentration ranges of 0.9 to 1200 mg·kg⁻¹ for Cu, 3.0 to 3820 mg·kg⁻¹ for Zn, 0.8 to 1070 mg·kg⁻¹ for Pb, and 18.2 to 1280 mg·kg⁻¹ for Cr [10]. Most of these evidently surpass the recommended critical minimum by the WHO [11]. Their presence is the main obstacle to the use of sewage solid waste in natural environment.

Soil as a major environmental component bears mechanisms for regulating excesses of otherwise toxic substances that may occur beyond the permissible limits as specified by WHO [11]. Such mechanisms include sorption (also known as adsorption) [12]. Sorption has been rated to attenuate heavy metal activity by levels of 22.22% to 99.25% [13]. Hence, this mechanism has potential to demobilise heavy metals from applied sewage solid waste for soil fertility management, and can be leveraged in making the stuff suitable for the purpose. In order to achieve maximum exploitation of this mechanism, there is a need for thorough understanding of its capacity, especially in the over-weathered soils of the tropics, whose negative charge is known to be restricted to the surface; and to be hypersensitive to pH changes [14].

Ferralsols, also often referred to as Oxisols, constitute over 60% of soils used for agriculture in the tropics [15] [16]. They possess low cation exchange capacity (CEC) and are high fixers of phosphorus (P), owing to their endowment with oxide and hydroxides of iron and aluminium [17]. When low in organic matter, Ferralsols reportedly can fix up 57% to 100% of applied P [17] [18] and thus deprive target crops of this important resource. However, their potential to sorb and desorb the most common heavy metals in sewage solid waste remains an issue for investigation. The objective of this study, therefore, was to examine the sorption and desorption phenomena of heavy metals in a Ferralsol as a result of application of sewage solid waste and phosphorus as soil fertility inputs.

2. Materials and Methods

2.1. Biosolid Waste Collection and Analysis

Four sewage solid waste samples, each of 5 kg, were collected in 10-kg capacity polythene bags from National Water and Sewerage Corporation (NWSC) treatment site at Bugolobi, in Kampala District, Uganda in January 2014. The sampling bags were pre-cleaned with concentrated spectroscopic nitric acid (about 50 mL), and rinsed three times with double distilled water (about 500 mL). The sewage solid waste samples were transferred to the soil laboratory where none organic materials such as stones, glass pieces, and plastic materials were sorted out. The remaining sewage solid waste samples were air-dried at room temperature (25°C) for 5 days. The stuff was ground into finer particles (<2.0 mm) using a porcelain mortar and pestle. The crushed sewage solid waste was kept at room temperature until laboratory analysis was carried out.

2.2. Experimental Soil

Soil sample (about 5 kg) was collected using a plastic spade, from a MUARIK cultivated field, sorted to remove visible materials such as roots, litter and stones. The sample was later air-dried on a clean polythene sheet under a shade, for 5 days. The soil was then pulverized using a porcelain mortar and pestle. Three sub-samples were taken for laboratory analysis using standard procedures [19] and the remaining bulk soil sample was kept for the sorption-desorption experiment.

2.3. Analysis of Sewage Solid Waste and Soil

The sewage solid waste and soil samples were both analysed for pH, organic matter, cation exchange capacity (CEC) and heavy metals (Zn, Cu, Pb and Cr). In addition, the sewage solid waste and the soil samples were analysed for total and available phosphorus respectively. The soil pH, total phosphorus and heavy metals (Cu, Zn, Cr and Pb) were determined using methods described by Page *et al.* [19]. Plant available phosphorus in soil was estimated using the Bray 1 extraction procedure [20]. Organic matter and cation exchange capacity of soil and sewage biosolid were determined by the Walkley-Black method and the ammonium acetate method [21] respectively.

2.4. Sorption-Desorption Experiment

Sorption-desorption experiment for the soil-sewage-phosphorous mixtures was done using the batch technique [22]. The input rates of sewage solid waste used were 0, 2.5, 5.0 and 7.5 metric tones biosolids ha⁻¹ on a dry weight basis; while those for the phosphorous fertiliser were 0, 25, 50 and 75 kg·Pha⁻¹. The experiment was carried out in polyethylene test bottles with treatments arranged in a completely randomized design in a factorial arrangement. Different heavy metals (chromium, copper, zinc and lead) each of concentrations of 25, 50, 100, 200, 400 and 500 mg·L⁻¹ were added to respective treatment combinations. These

concentrations covered the concentration range in the sewage solid waste samples.

The contents in polyethylene test bottles were shaken on a horizontal shaker, at 150 rpm for one hour for sorption or desorption equilibration to occur. The study was performed at room temperature $(25^{\circ}C)$ to simulate environmentally relevant field conditions. All treatments were carried out in triplicate and the experiment was repeated three times. The values obtained were used for further computation of sorbed and desorbed amounts. To obtain sorption and desorption isotherms, solutions of mixtures of Cr, Cu, Pb and Zn nitrates were prepared from stock solutions [22].

2.5. Data Analysis

The quality of the sorbent material is judged according to how much sorbate it can attract and retain it in an "immobilized" or fixed form. Thus, the calculation of metal uptake was based on the material balance of the sorption system as given in Equation (1).

$$Q_e = \frac{V(C_i - C_e)}{M} \tag{1}$$

where Q_e is the amount of metal sorbed per unit mass (mg·g⁻¹), V was the volume of the metal-bearing solution in litres; C_i and C_e are the initial and equilibrium (residual) concentrations (mg·L⁻¹) of the metal in the solution, respectively. *M* is the amount or mass of the amended sorbent (g) [12].

2.6. Langmuir and Freundlich Equations

A variety of models have been used to describe the sorption of ions by soils as a function of their concentrations in equilibrium solutions, but the most commonly used sorption equation is the Langmuir linear equation [23], *viz*:

$$\frac{C_e}{q_e} = \frac{1}{b} X_m + \frac{C_e}{X_m}$$
(2)

where C_e (mg·L⁻¹) is the equilibrium concentration of the species in the aqueous solution, q_e (mg·kg⁻¹) is the amount of sorbed species, *b* is a constant related to the bonding strength and X_m (mg·kg⁻¹) is the maximum sorption capacity.

The Freundlich sorption equation [24] is also commonly used in its linear form (Equation (3)):

$$\log q_e = \frac{1}{n} \log C_e + \log K_a \tag{3}$$

where K_a and $\frac{1}{n}$ are the Freundlich constants related to the adsorption capacity and intensity, respectively.

In the present study, both Langmuir and Freundlich equations were used to fit the data because they are common models used to study adsorption of heavy metals in aqueous solutions. The sorption and retention distribution coefficients of each metal in the sewage solid waste amended soil at equilibrium were calculated using the relation described by Covelo and others [22].

$$K_{da} \text{ or } K_{dr} = \frac{\left[C_a\right] \operatorname{or} \left[C_r\right]}{\left[C_e\right]}$$
(4)

where $[C_a]$ or $[C_r]$ is the concentration of sorbed/retained metal ions (mg·g⁻¹) and $[C_e]$ is the equilibrium concentration of the metal ions in solution (mg·L⁻¹) after sorption or desorption. The average distribution coefficient ($K_{d\text{-medium}}$) was used to obtain the overall selectivity sequences. It was calculated by adding either all values for sorption (K_{da}) or those for retention (K_{dr}) for a particular metal at all the concentrations considered and divided by their number [22].

Data collected were keyed into a Microsoft Excel, 7.0 spreadsheet and analyzed using ANOVA of the Statistical Package for Social Scientists (SPSS) version 17.0. Langmuir and Freundlich equations (Equation (2) and Equation (3)) were used to obtain the sorption and desorption isotherms. Standard multiple linear regression analysis was used to obtain the best fitting isotherms; and the method of least squares was used to find the Langmuir and Freundlich parameters or constants of the isotherms.

3. Results and Discussion

3.1. Heavy Metals in the Materials Used

Table 1 shows the laboratory results for the sewage solid waste and soil used in the sorption-desorption study. Sewage solid waste had significantly higher concentrations of heavy metals than the soil sample (**Table 1**). This was mainly attributed to industrial sources in the neighbourhood of the sewerage plant, where

Table 1. Characteristics of the	Kampala's sewage	solid waste an	d soil used in	the sorp-
tion-desorption study.				

Parameter	Sewage solid waste (mg·kg ⁻¹)	Soil sample (mg·kg ⁻¹)
pH (H ₂ O)	5.9	5.4
EC (dSm^{-1})	$10,000 \pm 12.0$	182.0 ± 4.9
CEC (cmolkg ⁻¹)	23.9 ± 1.4	8.7 ± 0.1
OM (%)	41.5 ± 3.8	2.51 ± 0.1
Ca	8448.0 ± 46.54	6.2 ± 0.12
Mg	1660.0 ± 64.81	1.55 ± 0.01
К	1584.0 ± 4.08	0.85 ± 0.01
Na	1500.0 ± 3.45	1.31 ± 0.01
N (%)	1.20 ± 0.11	0.14 ± 0.23
P (Bray 1)	7200.0 ± 15.8	2.86 ± 0.03
Cu	93.0 ± 3.2	10.0 ± 1.1
Cr	150.0 ± 3.7	131.25 ± 3.0
Pb	45.0 ± 4.3	12.75 ± 1.2
Zn	360.0 ± 10.2	1.34 ± 0.0

the metals are used as raw materials. The soil sample had almost the same concentration of Cr (131.25 \pm 3.0 mg·kg⁻¹) as the sewage solid waste (150.0 \pm 3.7 mg·kg⁻¹).

3.2. Competitive Sorption and Desorption

Results for sorption and desorption isotherms of heavy metals are presented in **Figure 1** and **Figure 2**. The illustrations are a plot of amount of each metal sorbed (Y-axis) against its initial concentration in the sorption solution (ISSC) (X-axis) or the quantity of each metal desorbed for each treatment at the end of the desorption stage, also against its initial sorption solution concentration (ISSC). Both experimental materials exhibited similar sorption/desorption trends for the four metals, regardless of the input rate used.

The results showed that sorption of the heavy metals (Cr, Zn, Cu, and Pb) increased as concentration of the cations increased in the sorption solution as displayed by **Figures 1(a)-(c)**. This is in agreement with observations of Reddy and Dunn [25]. This behaviour is probably attributed to the high organic matter content (about 41.5%) and the increased number of the metal ions available for the binding sites. The adsorbed heavy metal cations also help in further adsorption of more metal ions through cooperative adsorption [26] [27]. Additionally, metal adsorption is enhanced by the presence of phosphate on iron and aluminium oxide, clays and soil. In this study, the amended soil was a mixture of single

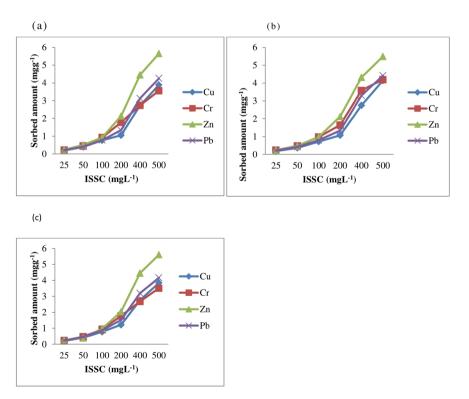


Figure 1. Amount of metal sorbed in the sorption experiment against its initial solution sorption concentration for sewage solid waste (a = 2.5 tones·ha⁻¹ + P-fertiliser 25 tones·ha⁻¹; b = 5.0 tones·ha⁻¹ + P-fertiliser 50 kg·ha⁻¹; c = 7.5 tones·ha⁻¹ + P-fertiliser 75 kg·ha⁻¹).

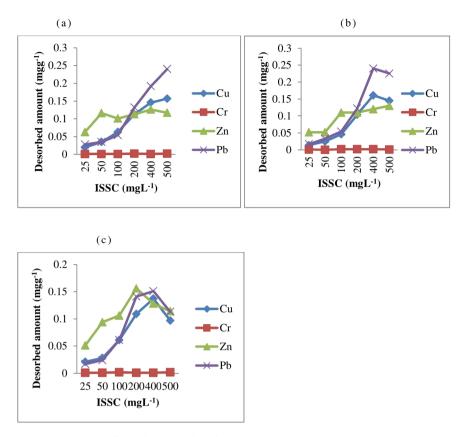


Figure 2. Amount of metal desorbed in the desorption experiment against its initial solution sorption concentration for sewage solid waste (a = 2.5 tones·ha⁻¹ + P-fertiliser 25 kg·ha⁻¹; b = 5.0 tones·ha⁻¹ + P-fertiliser 50 kg·ha⁻¹; c = 7.5 tones·ha⁻¹ + P-fertiliser 75 kg·ha⁻¹).

super-phosphate fertilizer and sewage solid waste which also contained phosphorous (about 7200 mg·kg⁻¹). The combined phosphorous could have led to the formation of metal-phosphate complexes and also metal-phosphate ion pairs. This could have led to increased bonding of both the metal and the phosphate to the adsorbent/amended soil.

In this study, the sorption isotherms of the four metals showed almost similar affinity for the binding sites at ISSC < 100 mg·L⁻¹; an indication that each metal possibly had an equal competitive opportunity to bind to the sites. Thus, at low metal loadings (<100 mg·L⁻¹) the metals were equally selected to bind to the sites. In contrast, at ISSC > 100 mg·L⁻¹, sorption of the metals demonstrated different abilities to compete for binding sites. The sorption after 200 mg·L⁻¹ could be attributed to multilayer sorption or clustering or precipitation, through electrostatic or non-specific sorption or cation exchange reactions as suggested by Sposito [28]; and specific sorption or non-electrostatic means as explained by Sparks [29].

Generally, desorption of Pb, Cu and Zn increased with increasing initial solution sorption concentration; while for Cr it was virtually irreversible (Figures 2(a)-(c)). Our results indicate that desorption of Pb, Cu and Zn decreased at ap-

plication rate ≥ 5.0 tones·ha⁻¹ of the sewage solid waste. This implies that use of sewage solid waste in Ferralsol at rates ≥ 5.0 tones·ha⁻¹ coupled with phosphorus fertilizer at a rate of ≥ 50 kg·ha⁻¹ will make all the metals investigated less available in solution phase and therefore in dismal amounts for plant uptake. Thus the chance to contaminate groundwater will also be limited.

Chromium was more retained than the other metals studied, at all input rates used (**Figures 2(a)-(c)**). The high sorption and retention of Cr could be attributed to the high charge-to-radius ratio of the metal ion (Cr^{3+}) [22] [30]. Chromium (III) has three arms that firmly bind on three negatively charged structures; yet the other metals (Cu (II), Zn (II) and Pb (II)) investigated have only two. The strongest bond is formed by the metal with greater charge-to-radius ratio on the basis of electrostatics [31]. The sizes of the ion radius and ion charge are most important when it comes to sorption and desorption (retention) of metals as explained by Bohn *et al.* [32].

Chromium has the smallest ionic radius and lowest pKa (0.061 nm, 4.0) values compared with all the other metals investigated; Pb (0.119 nm, 6.3), Cu (0.073 nm, 8.0) and Zn (0.074 nm, 9.0) [33]. These chemical properties make chromium (III) to easily form hydroxyl complexes compared to the other metals considered and thus, it is strongly sorbed and retained [34]. Chromium (III) ion, a strong Lewis acid, reacts strongly with oxygen-containing groups like OH⁻, COO⁻, O²⁻, CO²⁻₃, PO³⁻₄ and H₂O among others, which are Lewis hard bases found in biosolids and soil. Therefore, chromium (III) ion reacts more strongly with such groups than the divalent cations (Zn²⁺, Cu²⁺, and Pb²⁺) which are borderline Lewis acids, which ensures its retention.

3.3. Sorption and Desorption Linear Equations

Empirical Models and Fitted Isotherms

The experimental sorption and desorption equilibrium data of heavy metals on sorbent were fitted to Langmuir and Freundlich isotherm empirical models, which are usual models for aqueous-phase sorption [35]. The linear sorption and desorption isotherms adjusted better to Freundlich model than the Langmuir model; which is in conformity with the finding by [36] that heavy metal sorption isotherms are best described by the Freundlich equation at high metal concentrations. Accordingly, our discussion is centred on results obtained using the Freundlich model. From the linear Freundlich equation, correlation coefficient (r^2) , sorption/desorption intensity (n) and sorption/desorption capacity (K_a) values obtained at different treatment rates (T1, T2 and T3) are indicated in Table 2.

Generally, the four metals (Cu²⁺, Cr³⁺, Pb²⁺, and Zn²⁺) demonstrated ability to bind to sorption sites, as evidenced by values of *n* mostly being greater than one (0 < n < 10) (Table 2). A bigger *n* value indicates the ability of the metal to bind or attach to sorption sites [24] [35]. On the other hand, the values of *n* obtained were < 2, suggesting that sorbents used had surfaces with heterogeneously high-energy active sites [24]. For the sewage solid waste amended soil, Cr³⁺ had

Treatment	Metal	Freundlich constants and correlation coefficients					
			Sorption		Desorp		
		Ka	п	1 ²	K _a	п	r ²
T1	Cr	0.09	1.4	0.96	0.01	1.27	0.1
	Zn	0.04	0.71	0.72	0.011	0.93	0.9
	Cu	0.05	1.3	0.92	0.012	0.97	0.99
	Pb	0.06	1.22	0.95	0.014	1.02	0.98
T2	Cr	0.1	1.32	0.98	$2.3 imes 10^{-3}$	2.67	0.09
	Zn	0.03	0.67	0.93	$6.59 imes 10^{-4}$	0.33	0.4
	Cu	0.03	1.16	0.91	0.013	0.98	0.99
	Pb	0.06	1.23	0.93	0.013	1	0.99
T3	Cr	0.1	1.46	0.96	2.64×10^{-3}	3.73	0.02
	Zn	0.16	1.17	0.45	$8.97 imes 10^{-3}$	0.83	0.97
	Cu	0.06	1.31	0.92	0.013	1.05	0.95
	Pb	0.1	1.41	0.98	0.013	0.99	0.98

Table 2. Freundlich constants and correlation coefficient values for sorption and desorption for various heavy metals for sewage solid waste amended soil.

 $T1 = SSW (2.5 \text{ tones} \cdot ha^{-1}) + P \cdot \text{fertilizer} (25 \text{ kg} \cdot ha^{-1}), T2 = SSW (5.0 \text{ tones} \cdot ha^{-1} + P \cdot \text{fertilizer} (50 \text{ kg} \cdot ha^{-1}), T3 = SSW (7.5 \text{ tones} \cdot ha^{-1} + P \cdot \text{fertilizer} (75 \text{ kg} \cdot ha^{-1}).$

high values of K_a and n implying its possession of a high sorption capacity (binding energy) for the sites and sorption intensity, respectively (Table 2).

For desorption, K_a values indicated the relative ease of desorbing Cu²⁺ and Pb²⁺ compared to Cr³⁺ and Zn²⁺ (**Table 2**). In this case, Zn²⁺ and Cr³⁺ may have been specifically sorbed through formation of covalent bonds or by precipitation [37]. Thus, the K_a values obtained revealed the difficulty to desorb Cr³⁺ and Zn²⁺ from the study Ferralsol. This ultimately confirms the limited bioavailability of Cr³⁺ and its low chance of moving to contaminate groundwater.

 K_a values also provided information on how the metal ions (sorbate) were distributed between the soil solid phase and the soil solution phase [12] [35]. Big K_a values implied that the metal ions existed more in soil solid phase than in the soil solution phase. The large K_a values such as those obtained for Cr^{3+} , implied that the metal would be less available for plant uptake, and also will have limited chance to move into and contaminate groundwater.

3.4. Distribution Coefficients and Selectivity Sequences

The sorbed and retained equilibrium concentrations were used to calculate the distribution coefficients (K_d) (Table 3) using Equation (4) for the heavy metals (Cr, Zn, Cu and Pb) at the different study conditions. Generally, the results for sorption showed that the K_d values of the heavy metals decreased with increasing metal concentrations added and with increasing input rates.

The low sorption distribution coefficients (K_{da}) values at high metal concentrations of Cu, Cr and Pb in the initial test solutions were due to relatively low

			Treatment	s				
	Added	T1 T2			2	Т3		
	Concentration	K_{da}	K _{dr}	K_{da}	K _{dr}	K_{da}	K _{dr}	
Metal	$(mg \cdot L^{-1})$			(L	g ⁻¹)			
Cu	25	0.035	0.115	0.028	0.156	0.037	0.108	
	50	0.027	0.131	0.023	0.171	0.029	0.161	
	100	0.025	0.170	0.021	0.242	0.026	0.181	
	200	0.010	0.115	0.010	0.129	0.013	0.140	
	400	0.017	0.239	0.017	0.215	0.017	0.258	
	500	0.024	0.315	0.029	0.368	0.023	0.349	
Cr	25	0.043	4.050	0.061	3.922	0.048	4.878	
	50	0.043	5.425	0.059	8.492	0.047	8.241	
	100	0.046	14.254	0.060	15.415	0.047	15.70	
	200	0.037	25.676	0.028	23.137	0.037	25.62	
	400	0.017	40.753	0.034	43.477	0.016	34.82	
	500	0.018	46.316	0.030	58.270	0.018	50.05	
Zn	25	0.075	0.037	0.068	0.048	0.156	0.052	
	50	0.085	0.042	0.055	0.119	0.024	0.039	
	100	0.049	0.121	0.063	0.114	0.065	0.120	
	200	0.127	0.257	0.124	0.254	0.083	0.227	
	400	0.253	0.488	0.149	0.460	0.253	0.477	
	500	0.319	0.675	0.188	0.588	0.306	0.700	
Pb	25	0.048	0.087	0.054	0.158	0.082	0.157	
	50	0.032	0.131	0.036	0.144	0.047	0.220	
	100	0.026	0.240	0.029	0.238	0.039	0.220	
	200	0.016	0.129	0.016	0.142	0.023	0.137	
	400	0.024	0.205	0.029	0.169	0.026	0.279	
	500	0.032	0.221	0.038	0.248	0.030	0.315	

Table 3. Distribution coefficients (K_d) calculated for each metal concentration added at different input rates of sewage solid waste for the amended soil.

T1, T2 and T3 retain their earlier specifications.

sorption of their ionic species by the amended soil. It is likely that the amended soil exchange sites were fully saturated with Cu, Cr and Pb, to be able to sorb more. Similar results have been reported by [25]. The high values of K_{da} at high concentration of Zn in the initial test solution could also be a result of electrostatic sorption of the metal or a possibility of Zn-phosphate precipitate forming on Al and Fe-oxides [37], resulting from the total phosphorus added. The retention capacities (K_{dr}) of the metals increased with the rise in metal concentrations (**Table 3**).

The calculated average medium distribution coefficients ($K_{d\text{-medium}}$) were used to obtain the overall selection sequence of the metals and the results are given in **Table 4**. Generally, the selectivity sequences obtained for the aqueous medium used indicated that the concentration of metal in solution influences the sorption, desorption and selectivity processes. The selection sequence indicated that Cr was the most retained compared to the other study metals. Therefore, its leaching to groundwater is less probable for the study soil under the experimental condition used.

The results indicate that Zn and Cr were selected first among the metals investigated for sorption in the sewage solid waste amended Ferralsol (**Table 4**). This order implies that Cr would be least available for plant absorption and groundwater contamination; while Cu would be readily available. The sorption of the metals could be related to their electronegativity values – Zn (1.6), Cr (1.7), Pb (1.8) and Cu (1.9). Chromium was in the first place in all the retention sequences for sewage solid waste amended soil (**Table 4**). This is because it hydrolyses easily (low $pK_a = 4.0$) [33], making it to be specifically sorbed. Moreover, specifically sorbed metal ions are difficult to desorb [31]. The retention selection sequence which was in the order of Cr >> Zn > Pb > Cu, suggests that the charge-to-radius ratio is the most influential factor in retention of these metals.

3.5. Conclusion

The sorption and desorption of the heavy metals (Cr, Cu, Zn, and Pb) in the sewage solid waste amended Ferralsol increased with an increase in concentration of the various cations in the initial sorption solution concentration (ISSC). All the metals were less desorbed at high metal concentrations. The sorption and desorption isotherms adjusted better to the Freundlich model, which was attributed to heterogeneous nature of sorbent sites. Chromium was the most retained metal on the sewage solid waste amended Ferrasol due to its high charge-to-radius ratio. Desorption of the metals was found to be dismal thus, their ability to move and contaminate groundwater is limited and minimal amounts are expected to be phyto-available. Desorption of Pb, Cu and Zn decreased at

Table 4. Average distribution coefficients of metals between soil and solution ($K_{d-\text{medium}}$, Lg^{-1}) after sorption and retention, selectivity sequences when the sewage solid waste was used.

Treatment	Sewage	Cu	Cr	Zn	РЪ	Selectivity Sequence
T1	Sorption	0.022	0.140	0.058	0.043	Cr > Zn > Pb > Cu
	Retention	0.195	29.257	0.237	0.183	Cr > Cu > Zn > Pb
Τ2	Sorption	0.022	0.059	0.094	0.034	Zn > Cr > Pb > Cu
12	Retention	0.190	26.443	0.276	0.266	Cr > Zn > Pb > Cu
T3	Sorption	0.036	0.051	0.100	0.061	Zn > Pb > Cr > Cu
	Retention	0.177	34.087	0.316	0.221	Cr > Zn > Pb > Cu

T1, T2 and T3 retain their earlier specifications.

application rate ≥ 5.0 tones ha⁻¹ of the sewage solid waste. This implies that use of sewage solid waste in Ferralsol at rates ≥ 5.0 tones ha⁻¹ would make all the metals investigated less available in solution phase for possible plant uptake. The sewage solid waste can therefore be used to boost agricultural production as long as proper application rates are adhered to. The results indicate that there is limited chance for heavy metals to contaminate groundwater.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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